İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

ACTIVATION AND CHARACTERIZATION OF PHENOLIC BASED CARBON FIBERS

MSc Thesis by
Filiz KARADAĞ, BSc.
706021001

Science Programme: Advanced Technologies
Programme: Material Science and Engineering

Supervisors: Prof. Dr. Ekrem EKİNCİ
Prof Dr. M. Ferhat YARDIM

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PREFACE

In this study, the production and characterization of phenolic based activated carbon fibers have been reported. It was shown that process parameters such as activation time, activation media (gases), activation temperature and chemical treatment affect the properties (burn-off of activated carbon fibers, fiber structure, surface area, pore size distribution) of resultant ACF.

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CONTENTS

LIST OF TABLES

LIST OF FIGURES

ACTIVATION AND CHARACTERIZATION OF PHENOLIC BASED CARBON FIBERS

SUMMARY

Recent development of advanced materials technology has driven by the requirements for improved strength, low-weight and low cost in structural engineering materials. Carbon based materials have been used in high technology applications since 19^{th} century. The researches, which were made in late 1950's for producing high performance composite materials, have played a great role in the development of carbon fibers. These lightweight and high strength materials have led to significant advancements in industry.

Carbon fibers one of the key material positions among advanced carbon materials especially for composites and activated carbon fibers production. Although a wide range of materials have been used to produce carbon fibers since their introduction in early sixties, current commercial production is concerned on rayon, polyacrylonitrile, pitch, phenolic resin. The adsorption properties of activated carbon fiber (ACF) strongly depend on the nature of the precursors.

Activated carbon fiber is a microporous material consisting of three dimensional networks of micro graphitic layers. The huge surface area is one of the most important properties and also it has considerable amount of active functional groups. Exploitation of high surface area and reactivity of the functional groups of ACF is great benefit in adsorption mechanism especially, hydrogen storage devices.

In this study, two different processes were applied to the green phenolic based carbon fibers. The stage of the first process is the chemical treatment, carbonization and physical activation., the stages of the other process is carbonization and physical activation. For chemical treatment, stabilized carbon fibers were treated with chemical agents before carbonization. H_2SO4, HNO_3 and H_3PO_4 were used as chemical activators in present study. CO_2, steam and CO_2+steam mixture are the activation gases used for physical activation. Understanding the effect, of activation media, temperature and chemical treatment on ACF properties are investigated.

In order to determine the characteristics and structure activated carbon fibers are characterize by TGA, elementel analysis, FTIR and SEM. Adsorption properties of ACF are determined by using nitrogen, argon, hydrogen as adsorbate gas.

It is found that phenolic activated carbon fibers have narrow pore size distribution with micropore structure and have up to 3000 m^2/g surface area. CO_2+steam mixture is the most suitable activation gases for phenolic fibers. As the temperature increase the surface area of ACF increase and the chemical treatment does not affect

the surface area of ACF positively. It is found that ACF can adsorb hydrogen %3 weight.

FENOLİK BAZLI KARBON FİBERİN AKTİVASYONU VE KARAKTERİZASYONU

ÖZET

Gelişen teknolojiyle mukavemeti yüksek, hafif ve ucuz malzeme talebi, ileri teknolojnin doğmasina neden olmuştur. Karbon bazlı malzemelerin ileri teknolojilerde kullanımı 19. yüzyılın başına rastlar. Yüksek performanslı kompozit malzemelerin elde edilmesi için yapılan çalışmalar, kompozit malzemelerin hammaddesi ve karbon malzemelerin en onemlilerinden bir tanesi olan karbon fiberin gelişimine öncülük etmiştir. İleri teknolojiler için istenen yüksek mukavemet düşük spesifik ağırlık gibi ozellikleri bünyesinde barındırabilen karbon fiber oldukça geniş kullanım alanına sahiptir.

Kompozit teknolojisin ham maddelerinden bir tanesi olan karbon fiber ayrıca aktif karbon fiberin başlangıç malzemesidir. Karbon fiberler ticari olarak rayon, poliakrilonitril, zift ve fenol bazlı recinelerden üretilmektedirler ve aktif karbon fiber için en onemli özellik olan adsorbsiyon özelligi üretildiği malzemeye göre farklılık göstermektedir.Aktif karbon fiberin mikrogözenekli yapısı mikro grafitik ağ yapısı sayesinde oluşmaktadır. Amorf özellik gosteren aktif karbon fiberler de mevcutttur. Mikrogozenekli yapisı yuzey alaninin oldukça yüksek değerlere ulaşmasını sağlar.

Bu çalışmada fenolik bazlı karbon fiber hem fiziksel hem de kimyasal olarak aktive edilmiştir. Kimyasal aktivasyon icin H_2SO_4, HNO_3 ve H_3PO_4; fiziksel aktivasyon içinse CO_2, su buhari CO_2+su buhari karışımı kullanılmıştır. Aktivasyon gaz çesidi, aktivasyon sıcaklığı, kimyasal ajan deney parametreleri olarak incelenmiştir.

Üretilen aktif karbon fiberin karakterizasyonu TGA, elemental analiz, FTIR, SEM ile gerçekleştirilmiştir. Ayrıca adsorbsiyon özellikleri içinse azot, argon ve hidrojen gazları kullanılarak izotermler çıkarılmıştır.

Bu calismada fenolik bazlı karbon fiberden çesitli aktivasyon yöntemleri kullanarak yuzey alani 3000 m^2/g ulaşan ve mikrogozenekli yapiya sahip aktif karbon fiber elde edilmiştir. CO_2+su buhari karışımı kullanılan gazlar içinde en uygun aktivasyon ortamı olarak bulunmuştur. Sıcaklığın artması ile yuzey alanı artmaktadır. Kimyasal aktivasyonun yüzey alanı üzerinde olumlu bir katkısı olmadığı görülmüştür. Elde edilen aktif karbon fiberlerin kütlece % 3 hydrojen depolayabildiği saptanmıştır.

INTRODUCTION

Science and technologies focus on development of new and advanced materials. Carbon materials are characterized by high specific strength, low density, high conductivity which is according to carbon atoms. Moreover, carbon materials retain their good mechanical properties at high temperatures.

Carbon fiber is the one of the most important materials in carbon technologies. They are primarily used in composite technologies. More than 30 years have passed since commercially available carbon fiber appeared. Carbon fibers can be produced precursors such as rayons, polyacrylonitrile, pitch or phenolic resin. The properties of carbon fiber can be changed with precursor types.

Recently, activated carbon fibers have found many application areas. Their novel properties make them more attractive than conventional forms of activated carbons for certain applications. Being fibrous form they can be incorporated more easily into fabrics, filters, and other preforms. The chemical compositions of the fibers allow the creation of high specific surface areas in the region of 700-3000 m2/g. The fibers exhibit very high rates of adsorption and desorption .

This work was undertaken to develop and understand activation of the phenolic based carbon fibers. The present study consists physical and chemical activation of carbon fibers and determination of adsorption characteristic (Specific surface, average pore size and pore size distribution). In This study the hydrogen adsorption capacity of the produced activated carbon fibers is determined

2. GENERAL INFORMATION ABOUT CARBON AND CARBON FIBER

2.1. Carbon

Of all the elements, carbon is known as the most spacious studied and also it is one Latin Carbo, meaning charcoal, a material that is composed primarily of carbon [1]. The earliest use of carbon is as fuel in human history and its current applications cover areas as far as carbon fiber, composites and nanotechnologies etc. [2].

Carbon is the element number 6 of the periodic table of elements known by the symbol C, (electronic ground state $1s^2$ $2s^2$ $2p^2$) and has an atomic weight of 12.011 [3]. C^{12}, C^{13} and C^{14} are the three different existing isotopes of carbon. C^{12} accounts for about 98.89% of all carbon in nature. C^{13} has a natural abundance of 1.11 %, and the nucleus of C^{13} is magnetic, so it is being used in nuclear magnetic resonance spectroscopy (NMR) for identification of organic materials. C^{14} is radioactive, that is, its nucleus is unstable. Half-life of the C^{14} is about 5,730 years and knowing the original amount of C^{14} in organisms, thus the amount of C^{14} gives the time that passed since organisms died [4].

2.2. Carbon Structure

Carbon has four electrons in its valence shell (outer shell). Since this energy shell can hold eight electrons, each carbon atom can share electrons with up to four different atoms. Carbon can combine with other elements as well as with itself. This allows carbon to form many different compounds of varying size and shape. Over 500.000 carbon compounds have been identified. Carbon compounds can be synthesized in nature, or artificially produced in the laboratory. Carbon is found free in nature in many different structures called allotropes such as diamond, graphite, amorphous and fullerenes. Due to their different structures allotropes show different physical and chemical properties [5].

Diamond is the second most naturally occurring mineral form which was recognized as an allotrope carbon in the latter part of eighteenth century. Synthetic diamond like CVD diamond and octahedral diamond are not common. Diamond is one of the hardest known materials, least compressible substance known with the highest molar density; further each carbon atom bonds tetrahedral (sp^3) to four other carbon atoms to form a three-dimensional lattice and it is isotropic. Pure diamond is an electrical insulator—it does not conduct electric current. Diamond is also colorless, and because of its hardness, is used in industrial cutting tools. Figure 2.1 shows the structure of diamond.

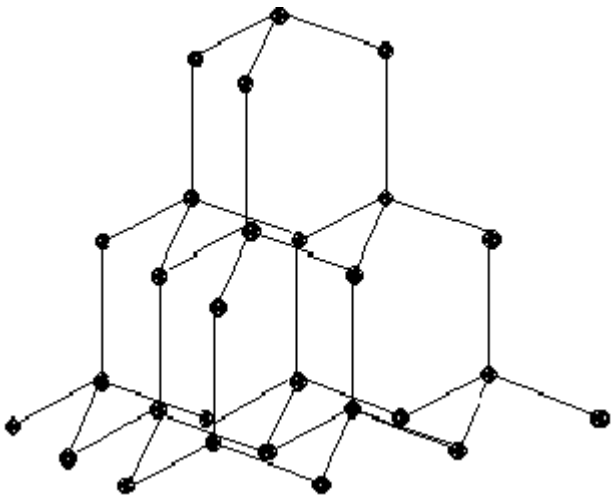


Figure 2.1: Structure of diamond [6]

Graphite is one of the softest known materials while diamond is one of the hardest. It is black, and conducts electricity. Moreover, in graphite, the atoms form planar, or flat, layers. Each layer is made up of rings containing six carbon atoms. The rings are linked to each other in a structure that resembles the hexagonal mesh of chicken wire. Each atom has three sigma bonds (with 120° between any two of the bonds) and belongs to three neighboring rings. The fourth electron of each atom becomes part of an extensive pi bond system. Graphite conducts electricity, because the electrons in the pi bond system can move around throughout the graphite. Bonds between atoms within a layer of graphite are strong, but the forces between the layers are weak [3]. Figure 2.2 shows graphite structure.

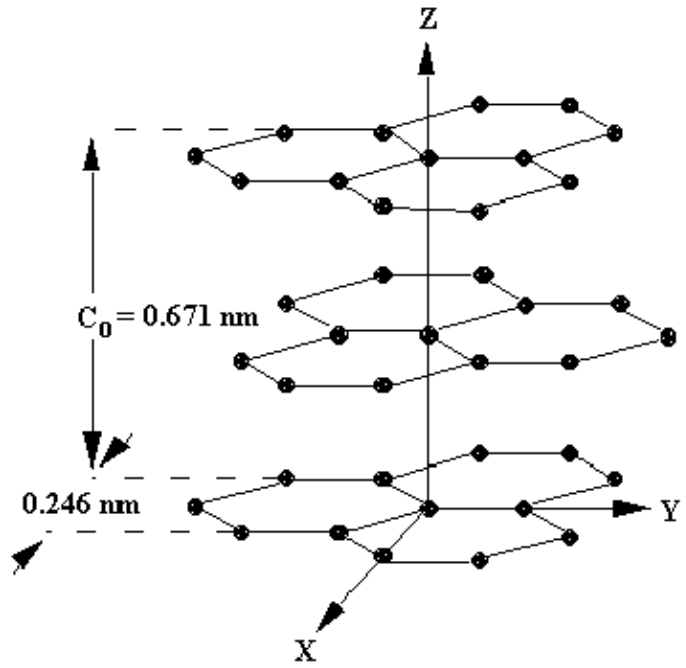


Figure 2.2: Graphite structure [6]

Third allotrope of carbon is fullerene that is found in 1985 (Figure 2.3). The original fullerene forms molecules of 60 carbon atoms (with a molecular formula of C_{60}), shaped like tiny soccer balls, with an atom at each point where the lines on a soccer ball would normally meet. Later, other fullerenes such as C_{70}, C_{76}, C_{78}, and C_{84} have been isolated. Fullerene is used in many ways such as they conduct electricity with no resistance and used as a superconductor [5].

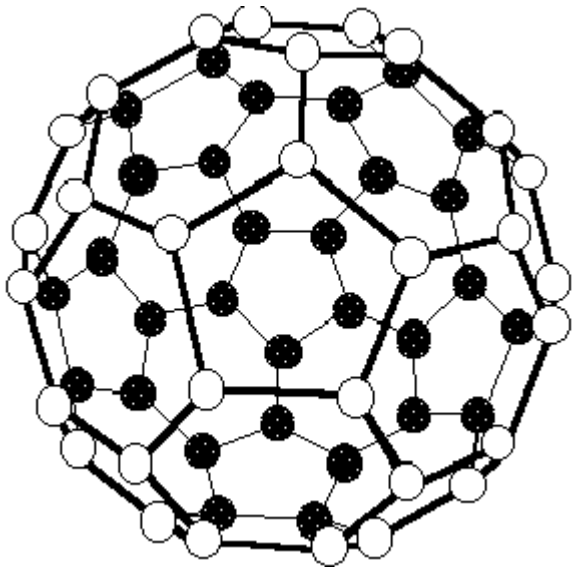


Figure 2.3: Fullerene structure [6]

Amorphous carbons are charcoal, coke, anthracite, bituminous coal, lignite etc. They are made up of tiny crystal-like bits of graphite with varying amounts of impurities. For example, the coal industry divides coal up into various grades depending on the amount of carbon in the coal and the amount of impurities. The highest grade, anthracite, contains about 90% carbon. Lower grades include bituminous coal, which contains 76% to 90% carbon, sub bituminous coal, with 60% to 80% carbon content, and lignite, with 55% to 73% carbon content [7].

2.3. Carbon Fiber

Carbon fibers, a kind of synthetic carbons, can be defined as strategic materials which have high modulus, high strength by weight, and high thermal conductivity Furthermore, carbon fibers have nearly zero coefficient thermal expansion [8]. Carbon fibers have about 92% carbon in their composition. Their structures consist of a disordered arrangement of small, two dimensional graphitic regions to partially crystalline, to disorganized amorphous regions (Figure 2.4) [9].

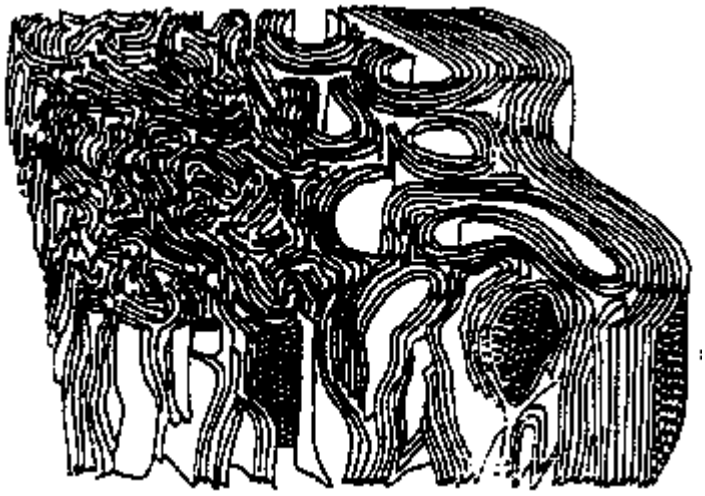


Figure 2.4: Schematic structure of carbon fiber structure [9]

It is well known that the mechanical properties of carbon fibers are improved by increasing the crystallinity and the orientation and by reducing the defects in the fibers [9]. In the graphitic lattice of carbon fiber structure, the carbon atom arranged in the hexagonal layers oriented parallel to the axis of fiber. The carbon atoms within the plane are covalently bonded each other, whereas those atoms that lie between the planes have only weak wan der waals forces between them (Figure 2.5). As a result

of this, carbon fibers have higher moduli along the fiber axis and much lower moduli perpendicular to the axis [10]. The degree of crystallinity present in carbon fibers can differ greatly as a result of the precursor materials and the processing conditions [12].

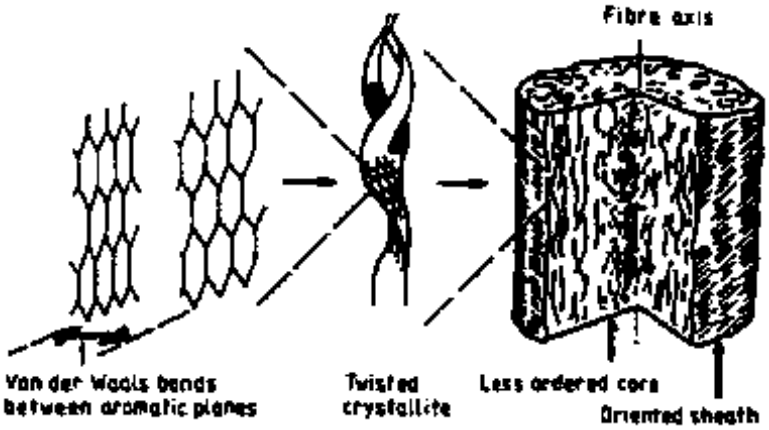


Figure 2.5: Carbon fiber structure [12]

Especially fibers are produced by subjecting organic precursors to a sequence of heat treatment. So, the precursor is converted to carbon by pyrolysis [13].

Today, carbon fibers are mainly used as filler materials for carbon-carbon composite materials, and also they are used as activated carbon fibers after extra processings [8].

2.3.1. History of Carbon Fiber

The existence of carbon fibers came into being in 1879 when Thomas Edison took out a patent for the manufacture of carbon filaments suitable for use in electric lamps. However, it was in the early of 1960's when successful commercial production was started, as the requirements of the aerospace industry- especially for military aircraft–for better and light weight materials became of paramount importance [13]. Cellulose was selected as the starting materials for carbon fibers because it has suitable thermosetting properties which keep of the fibers during subsequent heat treatment. However, adequate properties of cellulose based carbon fibers were not obtained until now. Although, Union Carbide Corporation first commercialized cellulose based carbon fibers, their production is very restricted because of limited properties and yield [8].

In the later sixties, PAN (Polyacrylonitrile) based carbon fibers which turned out to be more economical due to the less expensive precursor polymer and to the simpler fabrication process, the technical and commercial breakthrough for high performance fibers were developed [13].

In 1970's, some scientists successfully developed carbon fiber firstly from isotropic pitch later from anisotropic pitch. Then mesophase pitch based carbon fiber derived from petroleum commercialized [8].

In those years scientists and engineers were trying to find other precursors for carbon fiber production. At the end of 1970's, James Economy and coworker developed phenolic based resin fibers, and Kynol Corporation started to produce phenolic resin fibers commercially [15].

Lastly, whisker type of carbon fiber, called "vapor grown carbon fiber" are prepared by catalytic decomposition of hydrocarbon gases such as methane, benzene, or carbon monoxide on the metallic particles or surfaces. In 1972, Koyama and coworkers yield of vapor grown carbon fibers by thermal decomposition of benzene at about 1200 °C [16]. These types of fibers and chemical vapor deposition method have attracted more and more interest to prepare carbon fiber because of potentially low cost, large quantity and high mechanical performance [17].

Today in order to take advantage of carbon fibers for structural applications such as composite materials, and activated applications, research are being concentrated on developing suitable precursors and suitable process conditions.

2.3.2. Carbon Fiber Precursors, Types and Classifications

Carbon fibers can be classified in to different categorizes on the basis of precursor types, modulus, strength, and final heat treatment temperature of carbon fibers.

Carbon fibers are produced by using many precursors that are PAN, rayon, pitch (isotropic or mesophase pitch), gas-phase-grown carbon fibers and phenolic resin.

Specifically, any candidate precursor material should be easy to spin into fiber form without individual fibers adhering one another, decompose before melting (and at a reasonable slow rate). It should also provide a high carbon yield upon pyrolysis and have a high crystalline content with a high degree of preferred orientation along the fiber axis [12].

PAN based carbon fibers are obtained in three steps. In stabilization, polyacrylonitrile precursor is oxidized in a temperature range of 200-300°C. Thermoplastic PAN transform to a non-plastic cyclic or ladder compound with this treatment. In carbonization, fibers are carbonized at about 1000°C without tension in an inert atmosphere (normally nitrogen) for a few hours. During carbonization, the volatiles are removed as to give carbon fibers with a yield of about 50% of the mass of the original PAN. In graphitization, the fibers are treated at temperatures between 1500-3000°C which improves the ordering and orientation of the crystallites in the direction of the fiber axis.

Rayon based carbon fibers are also produced in three steps. In stabilization, firstly, physical desorption of water is realized between 25-150°C. The next step is a dehydration of the cellulosic unit between 150-240°C. Finally, thermal cleavage of the cyclosidic linkage and scission of ether bonds and some C-C bonds via free radical reaction (240-400°C) and, thereafter, aromatization takes place. In carbonization, between 400 and 700°C, the carbonaceous residue is converted into graphite-like layers. Graphitization is carried out under strain at 700-2700°C to obtain high modulus fiber through longitudinal orientation of the planes.

Production of carbon fiber from pitch can be described by following four steps. In pitch preparation an adjustment in the molecular weight, viscosity, and crystal orientation for spinning and further heating are made. In spinning and drawing step, pitch is converted into filaments, with some alignment in the crystallites to achieve the directional characteristics. In stabilization, some kind of thermosetting to maintain the filament shape during pyrolysis. The stabilization temperature is between 250 and 400°C. The carbonization temperature is between 1000-1500°C.

Both isotropic and anisotropic pitches can be used as a pitch precursor to carbon fiber.

The isotropic pitch or pitch-like material, i.e., molten polyvinyl chloride, is melt spun at high strain rates to align the molecules parallel to the fiber axis. The thermoplastic fiber is then rapidly cooled and carefully oxidized at a low temperature (<100°C). The oxidation process is rather slow, to ensure stabilization of the fiber by cross-linking and rendering it infusible. However upon carbonization, relaxation of the molecules takes place, producing fibers with no significant preferred orientation.

This process is not industrially attractive due to the lengthy oxidation step, and only low-quality carbon fibers with no graphitization are produced. These are used as fillers with various plastics as thermal insulation materials.

High molecular weight aromatic pitches, mainly anisotropic in nature, are referred to as mesophase pitches. The pitch precursor is thermally treated above 350°C to convert it to mesophase pitch, which contains both isotropic and anisotropic phases. Due to the shear stress occurring during spinning, the mesophase molecules orient parallel to the fiber axis. After spinning, the isotropic part of the pitch is made infusible by thermosetting in air at a temperature below its softening point. The fiber is then carbonized at temperatures up to 1000°C. The main advantage of this process is that no tension is required during the stabilization or the graphitization, unlike the case of rayon or PANS precursors [18].

Gas-phase-grown carbon fibers are a new class of carbon fiber that is distinctively different from other types of carbon fibers in its method of production, its unique physical characteristics, and prospect of low-cost fabrication. Gas-phase-grown carbon fibers may be produced in a two stage batch process where the length of the fiber can vary from about 100 micrometers to several centimeters or longer, and diameter up to 100 micrometers [19]. In the batch process the fibers are prepared by decomposition of hydrocarbon on a catalyst seeded substrate. Another production technique for Gas-phase-grown carbon fibers is floating-catalyst in a continuous-flow reactor. This one-stage technique produces fibers at much higher rate and at lower costs than the two stage process used for fiber. The pyrolysis of hydrocarbon in the presence of the catalyst results in the formation of a graphitic structure. The filaments are thus generated in the airborne configuration, and drift towards the gas exit driven by the reactant gas flow. As the fibers intersect in the gas stream they become tangled, thus resulting in an entangled mass of discontinuous randomly oriented fiber. Also, since the residence times are short in the continuous flow reactor, the fibers are usually less than 100 micrometers in length and 200 nanometers in diameter.

Before mentioning phenolic resin fiber the production of phenolic resins precursors should be explained. Phenolic resins are produced by the condensation of a phenol and an aldehyde.

Phenolic resins are generally classified as either resoles or novolacs. Resoles are ordinarily prepared by carrying out the condensation with a molar excess of the aldehyde and in the presence of an alkaline catalyst. Resoles are characterized by the presence therein of methylol groups, which render it possible to effect curing and cross-linking via methylene linkages by heat alone.

Novolacs are usually prepared by employing an acid catalyst and a slight molar excess of the phenol. Novolacs are characterized by the absence of methylol groups, and accordingly, they cannot be cured and cross-linked by heat alone, additionally requiring the presence of a source of methylene groups and preferably a suitable catalyst [20] , [24].

Thermoset phenolic resin fibers are a comparatively recent development in the history of phenolic resins. They are ordinarily produced by fiberizing a melt of a phenolic resin, as by melt spinning or by blowing (i.e., allowing a thin stream of the melt to fall into the path of a blast of a gas such as air which fiberizes the stream), to obtain thermoplastic uncured phenolic resin fibers. They are subsequently treated to cure, or cross-link, the resin at least to the point of infusibility. When the phenolic resin is selected as a resole, such curing is effected merely by heating. When the phenolic resin is selected as a novolac, curing is effected by heating in the presence of a source of methylene groups such as hexamethylenetetramine, Para formaldehyde or formaldehyde, and preferably also in the presence of an acidic or basic catalyst, hexamethylenetetramine being rather unique in being able to serve as both a methylene group source and a basic catalyst.

Fibers may also be prepared from mixtures of resoles and novolacs in any desired proportions, the curing conditions being selected with regard to the proportions. Additives and modifiers, either reactive or non-reactive, may be incorporated in the phenolic resin to alter its fiberization characteristics and/or the properties of the fibers.

Since phenolic resin fibers are infusible (thermoset) and have an inherently high carbon content of about 76wt%, they are excellent precursors for carbon fibers and textile materials. Either unprocessed tow or finished materials such as felt and woven fabric may be carbonized with high yield by simple one-stage high-temperature processing in an inert atmosphere, without the need for any pre-treatment or

application of tension during carbonization. Shrinkage of the material during carbonization is predictable and low (around 20%), and structural distortion is minimal.

Phenolic resin fibers are amorphous in structure and even treatment at the usual graphitization temperatures of 2000°C or higher do not results in the formation of the typical well-ordered graphite molecular structure [25].

Based on modulus and strength, carbon fibers can be grouped into:

- Ultra-high-modulus, type UHM (modulus >450 Gpa)
- High-modulus, type HM (modulus between 350-450 Gpa)
- Intermediate-modulus, type IM (modulus between 200-350 Gpa)
- Low modulus and high-tensile, type HT (modulus < 100 Gpa, tensile strength > 3.0Gpa)
- Super high-tensile, type SHT (tensile strength > 4.5 Gpa) [26].

Based on final heat treatment temperature, carbon fibers are classified into:

- Type-I, high-heat-treatment carbon fibers (HTT), where final heat treatment temperature should be above 2000°C and can be associated with high-modulus type fiber.
- Type-II, intermediate-heat-treatment carbon fibers (IHT), where final heat treatment temperature should be around or above 1500°C and can be associated with high-strength type fiber.
- Type-III, low-heat-treatment carbon fibers, where final heat treatment temperatures not greater than 1000°C. These are basically low modulus and low strength materials [26].

2.4. Activated Carbon Fiber (ACF)

Activated carbon fibers are amorphous carbon having played major role in adsorption technology. Typical properties of Activated carbon fibers are

- extremely high surface area
- adsorption capacities more than traditional carbon fibers
- tailorable mechanical properties [9]

Because of the above, ACF has much greater capacity and high speed in performing adsorption and desorption than that of powder and granule activated carbon [27].

Activated carbon fibers were first developed in the late 1960's and commercially produced in the early 1970's [13]. The raw materials for activated carbon fibers that are commercialized are phenol resin fibers, cellulose fiber, PAN fiber, and cloth or felt prepared from these fibers [28]. Physical properties comparison of different kinds of activated carbon fibers are given in Table 2.1.

Table 2.1 : Physical Properties of Different Kinds of Activated Carbon Fibers [29]

Properties	Phenolic resin	Cellulose	PAN	Pitch	Granular Activated Carbon (GAC)
Fiber Diameter(μm)	9-11	15-16	6-11	10-14	
Surface Area(m^2/g)	1000-2300	1000-1500	700-2000	1000-2000	800
Micropore Volume(ml/g)	1.0-1.2	0.2-0.7	1.5-2.0	0.2-0.7	0.001-0.01
Micropore Diameter(A)	0.5-1.2	0.4-0.6	0.4-1.0	0.5-1.0	0.3-0.5
Tensile Strength(kg/mm^2)	<20	<20	<20	<45	40-60
Tensile Elasticity(kg/mm^2)	30-70	7-10	20-50	10-18	
Elongation(%)	2.7-2.8		<2	2.4-2.8	
Ash content(%)	0.03-0.05	<1.0			
Toluene Absorption(%)	30-80	30-60	30-70		30-35
Iodine Adsorption(mg/g)	950-2200	>1300	>1500	1000-2000	
Methylene Blue Adsorption(ml/g)	310-380	>300	>300	250-350	70-80

General characteristics of activated carbon fibers can be explained below:

- High adsorption capacity: The adsorption capacities of activated carbon fibers are often larger than the traditional activated carbon about several to dozens of times for the organic vapor and odor material (n-Sulfur butanol). In addition, the adsorption capacity of ACF is especially excellent for the gases concentrations below ppm's [27].

- Very Speed Adsorption velocity: The adsorption velocities of activated carbon fibers are 10-100 times higher than the traditional activated carbon adsorption pollutant from gas phase. In other words, they can reach to the expectable efficiency in short time because of its low density.

- Being a best heat insulator: The ACF can exist upon 1000°C in inert gases and its ignition temperature in air is higher that 500°C.

- Good acid, and alkali resisting

- Very low total ash content

- Being a function of bacteriostasis [29]

Generally, activated carbon fibers are produced by pyrolysis of carbon in nitrogen or argon atmosphere, followed activation (pore and surface area formation) at a higher temperature in an oxidizing gas of air, flue gas, oxygen, carbon dioxide, or superheated steam [8]. However, the condition of activation is changeable with the process conditions. Figure 2.6 represents an example of the preparation procedure for active carbon fibers.

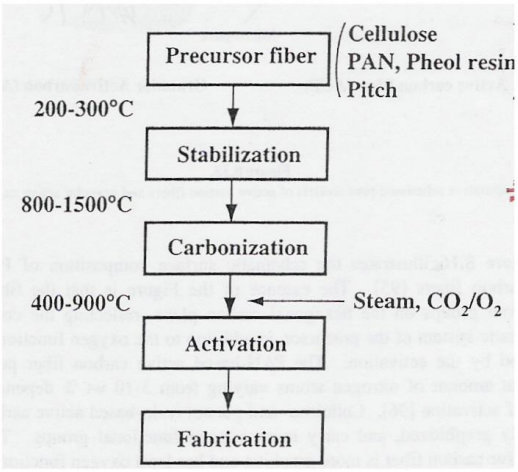


Figure 2.6 : Preparation procedure for activated carbon fibers [8]

The main steps for carbon fiber activation are stabilization, carbonization, and activation. Those steps are explained below.

2.4.1. Stabilization

A stabilization process is necessary to preserve the molecular structure generated as the fibers are drawn. This step is the slowest and rate-determining in the overall manufacturing process. Thus, it is very cost- effective process. Stabilization is performed in air, oxygen or other oxidizing agents at temperature 200-400°C and the controlling heating rate are very important, because this step is very exothermic. The purpose of this step is to oxidize of the surface of the carbon fiber due the fact that the surface oxygen group affects the step of carbonization and action of the carbon fibers. There are numerous reactions that occur during the stabilization process, like oxidation, cyclization, and saturated carbon dehydration. There are also some evidence that below 350°C , stabilization cause additional crosslinking that causes improved mechanical properties of carbon fibers [8][30][31].

2.4.2. Carbonization

Carbonization is the process that converts organic material to solid carbon as a main product and different volatile compounds as by products. Carbonization can also be defined as pyrolysis. It is controlled by some parameters. These are temperature, heating rate, residence time at the carbonization temperature, and the flow of inert gas [32].

The carbonization process is carried out between 600°C and 1000°C depending on the precursor types in a continuous stream of an inert gas. Especially, the basic microstructure was formed by 500°C. Although, some of pores are blocked by some pyrolysis products and could become available only when high temperature treatment was given [33].

The factors that affect carbonization also have a marked influence in activation and on the quality of the final product [33].

2.4.3. Activation of Carbon Fiber

The objective of activation can be explained as to enlargement of the volume and enhancement of the diameters of the pores which were created during the carbonization process and create some new porosity. The structure of the pores and their pore size distribution are largely predetermined by the precursor material of carbon fiber and the carbonization conditions.

Activation of carbon fibers can be divided into three steps. First, the activation removes disorganized carbon, exposing the aromatic sheets to the action of activation agents in the first phase and leads to development of a microporous structure. Later, the reaction affects widening of existing pores and an increase in the transitional pores and macroporosity [33].

Activation process can be divided into three main types according to media of activation.

1- Physical activation

2- Chemical Activation

3- Mixed approach of physical activation of chemical preactivated sample [32].

2.4.3.1. Physical Activation

Physical activation process is performed by using CO_2, steam, air or any mixture of those gases. Physical activation of carbonaceous material involves both physical and chemical processes. The physical process is removing of volatiles condensed in the pores by the flow of the activating gas. As a result of diffusion of activating gas into carbonaceous material, there is an increase in the volume of the porous structure. Chemical process in physical activation is the interactions of the activating gases with carbon, which can be shown by the following reactions [33], [31].

$C + O_2 \longleftrightarrow CO_2 + 348\ KJ$

$2C + O_2 \longleftrightarrow 2CO + 226\ KJ$

$C + H_2O \longleftrightarrow CO + H_2 - 130\ KJ$

$C + 2H_2O \longleftrightarrow CO2 + 2H_2 - 97\ KJ$

$C + CO_2 \longleftrightarrow 2CO - 163\ KJ$

It was found that

a- CO_2 generates narrow pore size distribution

b- The diameters of the fibers decreased in the first stage of the activation and after that remained nearly constant

c- Tensile strength decreased during the whole burn-off range studied [32].

On the other hand steam has different effects;

a- wider pore size distribution

b- the diameters of the fibers decrease with burn-off

c- tensile strength decreases little with burn-off [32].

Steam carries external fiber burn-off leading a widening of pore size distribution and reducing fiber diameter. On the other side, CO_2 makes microporosity without changing the fiber diameter as a result of creating porosity throughout the fiber, not only on the external surface [32].

In the case of activation with oxygen, the process is exothermic, so there is excessive burning and reaction is difficult to control, local overheating is encountered.

2.4.3.2. Chemical Activation

Chemical activation is the process that uses chemical agents to produce dehydration effect [33]. H_3PO_4 (phosphoric acid), $ZnCl_2$ (zinc chloride), H_2SO4, HNO_3 are the most used chemical activators for activation of carbon fibers [8].

The activation process can be summarized that carbon fiber is firstly impregnated with the activating agent in the form of the concentrated solution usually by mixing or kneading. Then chemical impregnated material is than extruded and pyrolyzed in an inert atmosphere at 400-600°C. The pyrolyzed product is cooled and activating agent is removed [33].

The previous condition of chemical activation is the pressure at non-carbonized regions in the carbon fiber, which are capable of being destroyed or volatilized by the activators. The activation process is primarily directed at freeing and sealed micropores of the volatiles, thus forming channels for the evaluation of volatile products [32].

To contrast physical activation, chemical activation is not characterized by the burn-off of the carbon fiber. So that the adsorption capacity of such adsorbent is lower than the physical activation. The advantageous of the chemical activation are high yield of the activated material and a short duration of the activation [32].

2.4.3.3. Mixed Approach of Physical Activation of Chemical Preactivated Sample

In some processes for carbon fibers, physical activation may be applied after chemical activation. Chemical activation increases the yield of activated material. On the other hand, physical activation increases the pore size distribution. So, both chemical and physical activations can be assembled to make high yield of activated carbon fibers and high pore size distribution activated carbon fibers [9].

Because of the properties of the activated carbon fiber like large adsorption capacities and rates, along with their electric and magnetic properties make them enable to a variety of adsorbent and other applications [9]. So the studies that are related to activation of carbon fibers have continued in the literature since 1960's. To summarize, activated carbon fiber type are influenced by precursors of activated carbon fiber. Though, the final products of activated carbon fiber can be varied by the processing conditions. It can be said that heating rate, final temperature, activation type, and length of the activation period are the factors for the pore volume, surface area, and mean pore diameter of the activated carbon fibers [31] .

2.5. Adsorption Theory

Adsorption is a surface phenomenon. It is defined as an increase in the concentration of a particular component within interfacial region separating two phases [34]. Adsorption can take place at liquid-liquid, gas-liquid, solid-solid, gas-solid and liquid-solid interfaces.

There are some other terminologies that are used in adsorption theory.

Substrate - frequently used to describe the solid surface onto which adsorption can occur; the substrate is also occasionally referred to as the adsorbent.

Adsorbate - the general term for the atomic or molecular species which are adsorbed (or are capable of being adsorbed) onto the substrate.

Coverage - a measure of the extent of adsorption of a species onto a surface [34]

Adsorption is classified in two types depending on the molecules or atoms attachment to the surface of materials. Physical adsorption involves only relatively weak Wan der Waals inter molecular forces which formed a reversible adsorption equilibrium, and chemical adsorption as known chemisorptions involves the formation a chemical bound between the adsorbate molecule and the surface of the adsorbent. Although, the classification of adsorption is useful, there are many intermediate cases and it is not usually possible to segment a particular system [35]

The general properties of physical and chemical adsorption are shown in Table 2.2 [35], [36]

Table 2.2: General Properties of Physical and Chemical Adsorption

	Chemisorption	**Physisorption**
Temperature Range (over which adsorption occurs)	Virtually unlimited (but a given molecule may effectively adsorb only over a small range)	Near or below the condensation point of the gas (e.g. Xe < 100 K, CO_2 < 200 K)
Adsorption Enthalpy	Wide range (related to the chemical bond strength) - typically 40 - 800 kJ mol^{-1}	Related to factors like molecular mass and polarity but typically 5-40 kJ mol^{-1} (i.e. ~ heat of liquefaction)
Crystallographic Specificity (variation between different surface planes of the same crystal)	Marked variation between crystal planes	Virtually independent of surface atomic geometry
Nature of Adsorption	Often dissociative May be irreversible	Non-dissociative Reversible
Saturation Uptake	Limited to one monolayer	Multilayer uptake possible
Kinetics of Adsorption	Very variable - often an activated process	Fast - since it is a non-activated process

2.5.1. Physical Adsorption

The forces in physical adsorption are Wan der Waals [38] and electrical interactions comprising polarization, dipole and quadruple. The Wan der Waals has a longer range but relatively strength when a part is physical adsorbed on the surface it release small enthalpy change. This energy change is not enough to lead to band breaking; so, a physical adsorbed molecule retains its identity. Electrical interaction occurs in ionic structure. However, in adsorption of small dipolar molecules (H_2O or NH_3), the electrostatic contribution may be very large, giving rise to regarded as physical [35] , [37], .

Some features which are useful in recognizing physical adsorption include:

(a) the phenomenon is a general one and occurs in any solid/fluid system, although certain specific molecular interactions may occur, arising from particular geometrical or electronic properties of the adsorbent and/or adsorptive;

(b) evidence for the perturbation of the electronic states of adsorbent and adsorbate is minimal;

(c) the adsorbed species are chemically identical with those in the fluid phase, so that the chemical nature of the fluid is not altered by adsorption and subsequent desorption;

(d) the energy of interaction between the molecules of adsorbate and the adsorbent is of the same order of magnitude as, but is usually greater than, the energy of condensation of the adsorptive;

(e) the elementary step in physical adsorption from a gas phase does not involve an activation energy. Slow, temperature dependent, equilibration may however result from rate-determining transport processes;

(f) in physical adsorption, equilibrium is established between the adsorbate and the fluid phase. In solid/gas systems at not too high pressures the extent of physical adsorption increases with increase in gas pressure and usually decreases with increasing temperature. In the case of systems showing hysteresis the equilibrium may be metastable;

(g) Under appropriate conditions of pressure and temperature, molecules from the gas phase can be adsorbed in excess of those in direct contact with the surface (multilayer adsorption or filling of micropores) [37].

2.5.2. Chemical Adsorption

Chemisorption is a chemical bond, involving substantial rearrangement of electron density, is formed between the adsorbate and substrate. The nature of this bond may lie anywhere between the extremes of virtually complete ionic or complete covalent character [9][35][36][37] [38].

Some features which are useful in recognizing chemisorption include:

(a) the phenomenon is characterized by chemical specificity;

(b) changes in the electronic state may be detectable by suitable physical means (e.g. u.v., infrared or microwave spectroscopy, electrical conductivity, magnetic susceptibility);

(c) the chemical nature of the adsorptive(s) may be altered by surface dissociation or reaction in such a way that on desorption the original species cannot be recovered; in this sense chemisorption may not be reversible;

(d) the energy of chemisorption is of the same order of magnitude as the energy change in a chemical reaction between a solid and a fluid: thus chemisorption, like chemical reactions in general, may be exothermic or endothermic and the magnitudes of the energy changes may range from very small to very large;

(e) the elementary step in chemisorption often involves an activation energy;

(f) where the activation energy for adsorption is large (*activated adsorption*), true equilibrium may be achieved slowly or in practice not at all. For example in the adsorption of gases by solids the observed extent of adsorption, at a constant gas pressure after a fixed time, may in certain ranges of temperature increase with rise in temperature. In addition, where the activation energy for desorption is large, removal of the chemisorbed species from the surface may be possible only under extreme conditions of temperature or high vacuum, or by some suitable chemical treatment of the surface;

(g) since the adsorbed molecules are linked to the surface by valence bonds, they will usually occupy certain *adsorption sites* on the surface and only one layer of chemisorbed molecules is formed (monolayer adsorption) [37] [38]

2.5.3. Adsorption isotherms

The adsorption isotherm is a plot of the adsorbate which is adsorbed per unit weight or volume of adsorbents, as a function of the wide range of relative pressure at constant temperature and at equilibrium conditions [9][36][38].

The isotherms for physical adsorption divided into five classes as shown in Figure 2.7.

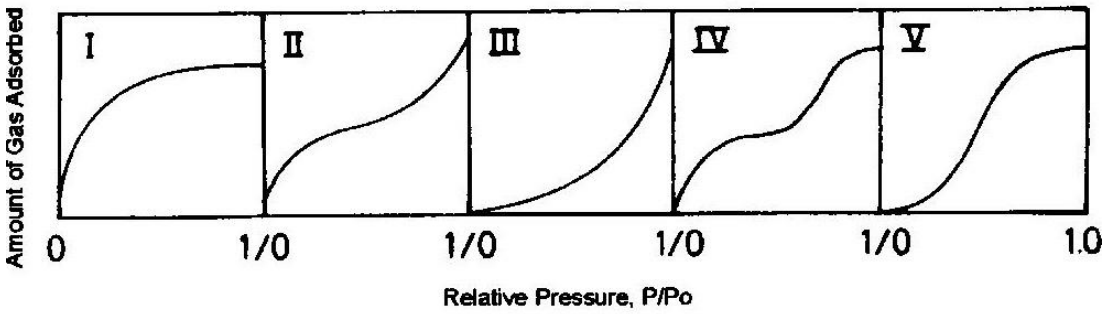


Figure 2.7: Adsorption Isotherms [35], [38],[39]

Type I isotherms show that high amount of adsorption at low pressure and the isotherm is the characteristic for monolayer adsorption. They are considered as favorable isotherms. Type I isotherms are exhibited by microporous absorbent in which the pore size is not very much greater than the molecular diameter of the adsorbate molecule. Type I is exhibited in chemisorption where the asymptotic approach to a limiting quantity indicates that all of the surface site are occupied [9], [38].

A gas molecule when encounters the overlapping potential from the pore walls which enhance the quantity of gas adsorbed at low relative pressure. At higher pressure, the pores are filled by adsorbed or condensed adsorbate, indicating little and additional adsorption after the micropores have been filled.

Type II isotherm are the form of the non porous or microporous adsorbent. This type of isotherm represents unrestricted monolayer-multilayer adsorption. In type II isotherm, there is a continuous progressing show that monolayer coverage is complete than the multilayer adsorption and to capillary condensation. The increase

in capacity is the result of capillary condensation in pores increasing diameter of the pressure is raised.

Type III isotherm are rarely encountered. The absence of an inflection point is caused by stronger absorbate-adsorbate than adsorbate-adsorbant interactions.

Type IV isotherms occur when the surface is homogeneous. The initial part of type IV isotherm is follows the some path as the type II. Type IV isotherms are associated with capillary condensation in mesopores, indicated by the step slope at higher relative pressures.

Type V isotherms are uncommon and associated with mesoporosity, usually exhibit mysteries between the adsorption and desorption isotherms [9], [38] .

2.6. Adsorption Properties of Activated carbon fibers

Adsorption properties of the porous materials depend on

- Pore size
- Shape
- Chemical nature of the pore [40]

Pore size can divide into three groups:

Pores with openings exceeding 500 Angstroms in diameter are called “macropores”

Pores with diameters not exceeding 20 Angstroms are called “micropores”

Pores with $20<x<500$ Angstroms are called “mesopores” [38]

An adsorption on a micropore with a diameter less than twice that of the adsorbate molecule achieves by the overlapping of interactive potential of both sides of the pore walls [41]. This mechanism is called filling mechanism by this mechanism, microporous adsorbents can adsorb a large amount of vapor in their microstructure [41].

The shape of pore is also important. It is found that the carbon microporous structure has of a tangled network of defect containing carbon layers. The micropores are between the space and the layer planes [43]. This structure affects the diffusion into microporous network.

Instead filling mechanism, the chemical structure of the activated carbon fiber also play an important role in adsorption capacity. Dispersion forces, random ordering of imperfect aromatic sheets and the presence of heteroatom in the activated carbon fiber cause in the creation of unsaturated valences and unpaired electrons, which influence the adsorption behavior [35]

2.7. Application Areas of Activated Carbon Fiber

Active carbon fibers are attractive in a number of advanced technologies. Special advantages of ACF over more established particulate active carbons include generally high adsorption capacities, magnetic and electrical properties, and faster adsorption/desorption rates.

2.7.1. Main Application Areas

Main application areas of activated carbon fibers can be divided in four groups

- Environmental applications
- Medical Clothing applications
- Electrical applications
- Catalysis [32]

2.7.1.1. Environmental Applications

Environmental applications are one of the main uses of activated carbon fibers.

Air cleaning and odor control: The odors in the indoor air includes ammonia, amine, and trimethylamine, sulfur methanol, hydrogen sulfide etc., Using ACF as adsorption material removes and deodorize more efficient, and also removal particles and moistures existing in the air, particularly aromatics and aryl substance which will generate carcinogens.

Water purification: ACF is widely used as color and odor removing material in the production of foods, medicines, beverages, sugars and wines. It is an ideal material as purifying medium in the production of drinking water and super pure water for industrial use [27], [44].

Wastewater treatment: ACF is particularly suitable for treating the wastewater contaminated by Phenol, and other chemical agents which have been preliminarily reduced to a certain level by biological technology. ACF has property of fast, high adsorption capacity, and easy regeneration, and ACF can reduce the cost of installation and avoid second pollution [29].

Solvent recovery systems: ACF can be used in solvent recovery from air stream such as the vapors of benzene, ketone, ester, and petroleum (particularly for the corrosive chloride, solvents of high reactivity and low boiling- point solvents). The speed of adsorption and desorption are fast, and the percentage of recovery can be reached to 97% [27], [29].

Gas purification systems;

- **Active carbon fibers in SO_x/NO_x removal from air**

An application specific to carbon fibers, is removal of SO_2, NO and NO_2 from the atmosphere as well as from flue gas. ACF may remove contaminants by catalysis, *e.g.,* by forming sulfuric acid from SO_2 in moist air, or by the selective catalytic reduction of NO/NO_2 to N_2 and steam in the presence of ammonia. ACF may also react with NO/NO_2 to yield N_2 and CO_2. These reactions need high surface area so ACF has one of the highest surface areas. Clearly it might have advantages over traditional active carbons in both these areas [44].

- **Active carbon fibers for removing volatile organic compounds from air**

Volatile organic compounds, VOCs, comprise generally toxic, low boiling point compounds, including aromatics such as toluene (methylbenzene) and the xylenes (dimethylbenzenes), and aliphatics, such as acetone (propanone) and *n*-hexane. Low concentrations of VOCs in ambient air of 1 to 1,000 ppmv (parts per million based on volume) are often harmful to human health. VOCs also promote the photochemical formation of ozone and other contaminants, and in high concentrations is a fire hazard. ACF especially phenolic resin fibers have been suggested to remove these volatile organic compounds [44][45][46][47].

2.7.1.2. Medical and Clothing Applications

Activated carbon fibers are used in some medical applications. Medical applications of ACF include cloth form as wound dressings and skin substitutes. ACF appear to be useful due to their high adsorption capacities and rates for low and medium molecular weight organic compounds in aqueous solution compared to granular active carbons. The ease of containment and formability of dressings based on ACF are also positive attributes. The apparent biocompatibility of ACF is another advantage in these applications [44]. Activated carbon fibers can also be used in the treatments of some liver ailments. Due to the adsorption properties, activated carbon fibers can eliminate cholesterol and lipo proteins in human body. Medical bandage, women pad and gas masks are other medical applications for ACF [32].

2.7.1.3. Electrical Applications

Other application of ACF is in electrical double-layer capacitors, storage battery and electric materials (Figure 2.8) [27].

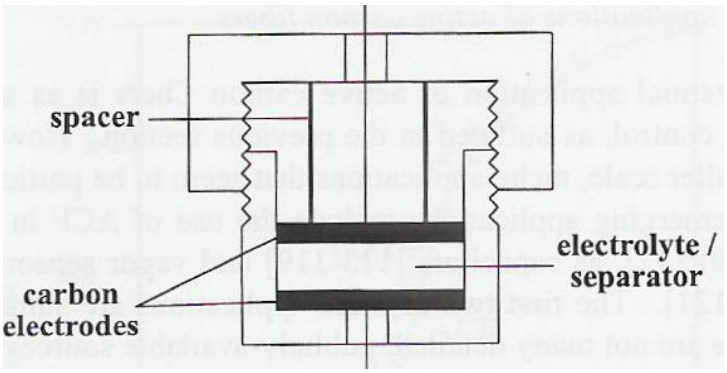


Figure 2.8: Carbon Electrodes in Double-layer Capacitor [44]

Capacitors using phenolic-based ACF and active fiber cloths, and incorporating both liquid and solid electrolytes, have received considerable attention in Japan for applications such as computer memory back-up devices. Perceived advantages of ACF include relatively high surface areas and electrical conductivities, and ease of formability and containment [44].

2.7.1.4 Catalysis

Activated carbon fibers are known as efficient catalysts or supports for the catalytically active phase in heterogeneous catalysis. The highly developed specific surface area, the probability of producing the materials with homogeneous surface properties make activated carbon fibers of catalytically active phase.

Beside other advantageous activated carbon fibers are used as heat conductance in catalysis processes, and electrical conductance in promoting electrocatalytic processes [32].

2.7.2. Some Examples of Commercial Applications

2.7.2.1. ACF for NBC Protective Technology

ACF is a unique patented fabric. Its unique 1.5nm~2nm width slit-shaped micropores have been proven in adsorption against traditional activated carbon. This gives ACF fabric a peerless performance for rapid and efficient adsorption of lethality molecules.

Due to the high efficiency in adsorption performance, new generation NBC protective cloth can be more air-permeable when using ACF fabric as a NBC filter. The fabric is fully suitable for NBC protective suits used in countries with hot climates, especially with missions in deserts. Also, ACF fabric grants permeable protective suits a lighter weight, so forces exert less physical strength carrying its weight, allowing more active movement during missions (Figure 2.9).

The 100% activated carbon in textile has no shedding problems as with granular or powder activated carbon through ageing or forming; guaranteeing its performance remains excellent, even after years' of storage [47].

Figure 2.9: NBC Protective Suits Preform Made with ACF [47]

2.7.2.2 The Water Purifier Filtering Slice

ACF is the main material of ACF filter. It is put in respirator or water clarifier to get rid of smell, bacterium, and dust (Figure 2.10) [49].

Figure 2.10: ACF Filter [49]

2.7.2.3 Active Carbon Fiber Paper

Active Carbon Fiber Paper, made of active carbon fiber with carrier added, possesses the functions as active carbon fiber has and the outstanding features as high strength, not easy to powderize , easy to be processed into various forms such as honeycomb and filter bar (Figure 2.11) [29] [49].

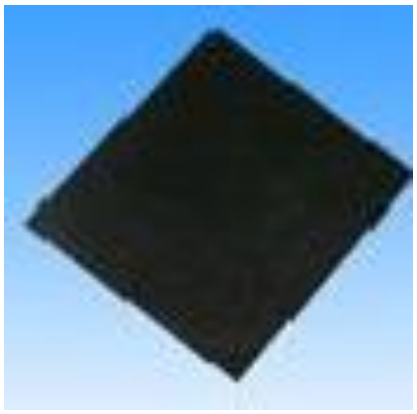


Figure 2.11: ACF Paper [49]

2.7.2.4 Activated Carbon Fiber Health Mattress

The activated carbon fiber health mattress has excellent functions such as moisture removal, peculiar smells elimination, warm-keeping, disinfecting etc. and can be widely used in hospitals, the aged welfare homes, families, hotels and ships etc. It can be used as health and clean-keeping bedding for the old, infants and patients lying in bed for longtime (Figure 2.12) [29] [49].

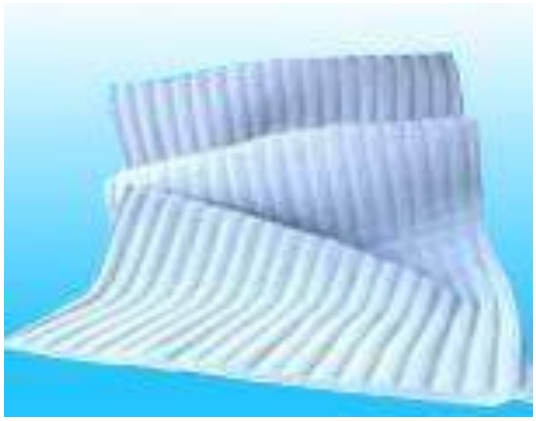


Figure 2.12: ACF Mattress [49]

2.7.2.5 Activated Carbon Fiber Insole

ACF may be used as insole. Wearable and comfortable, it also can adsorb sweat, deodorize and disinfect. Over a long period of time, insole will take effect as prophylaxis and treatment of the peculiar smell and ringworm of the foot (Figure 2.13) [49].

Figure 2.13: ACF Insole [49]

3. EXPERIMENTAL

In this section, properties of the phenolic resin based carbon fibers, experimental set up, and characterization equipments for the production of activated carbon fibers are given.

3.1. Phenolic Resin Fiber for Activated Carbon Fiber Production

In this study, phenolic resin based carbon fibers (Figure 3.1) from Gumma University of Japan were used. Carbon fibers are produced from condensation reaction of phenol and formaldehyde, and stabilized.

Figure 3.1 : Phenolic Resin Based Carbon Fiber

The production process of the phenolic fiber resin is explained in section 2.3.2. The structure of the phenolic resin based carbon fiber is given in Figure 3.2, and the properties of phenolic resin fiber are also presented in Table 3.1.

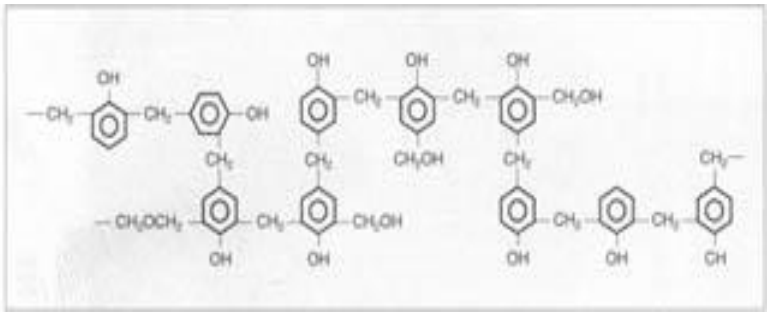


Figure 3.2 : Structure of the Phenolic Resin Based Carbon Fiber [25]

Table 3.1 : Properties of Phenolic Resin Based Carbon Fiber [25]

Color	gold
Diameter(micrometer)	14~33
Fiber length(mm)	1~100
Tensile strength(kg/mm^2)	<20
Solubility water, acid…	insoluble

3.2. Experimental Setup

The experimental setup for activation of carbon fibers is given in Figure 3.3.

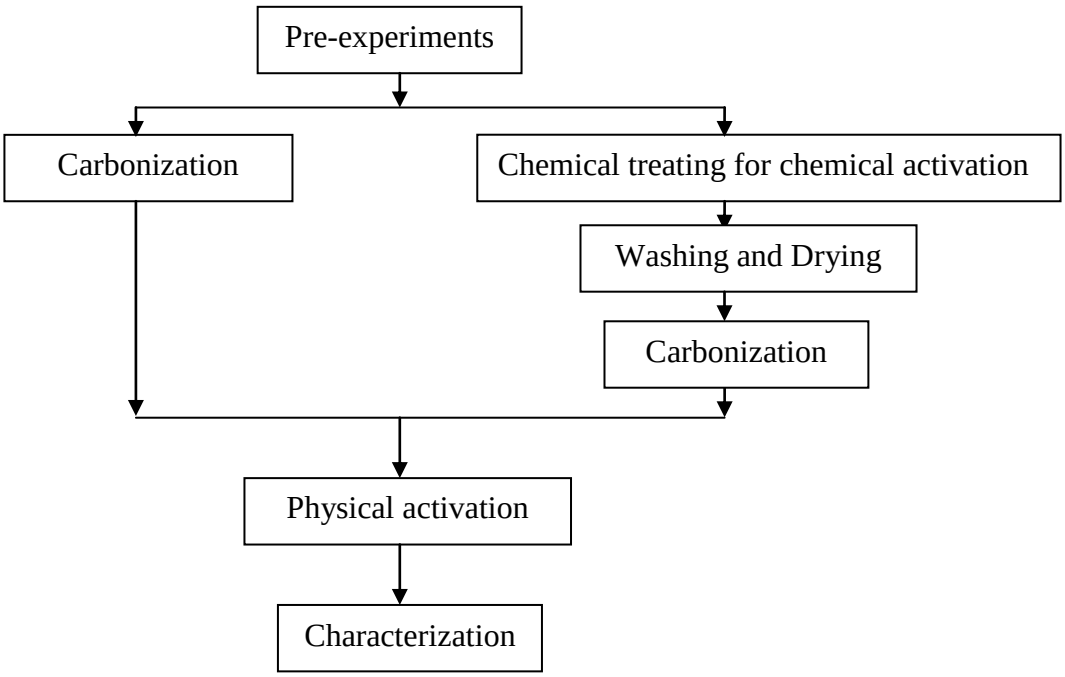


Figure 3.3 : Schematic Representation of the Experimental Setup

Before starting the main experiments, some pre-experiments were done using carbon fibers. For this purpose, carbon fibers were washed with ethanol and methanol in soxhlet system, in order to understand whether it has wax layer or not. After washing, TGA analysis was carried out on the green carbon fiber, methanol washed carbon fiber and ethanol washed carbon fiber.

After pre experiments, two different process were applied to the carbon fibers. One of these processes is the chemical treatment, carbonization and physical activation of the carbon fibers, while other process is carbonization and physical activation.

For chemical treatment, stabilized carbon fibers were treated with chemical solutions before carbonization. H_2SO4, HNO_3 and H_3PO_4 were used as chemical activators in present study. For chemical treatment 25 grams of H_2SO_4, 25 grams of P_2O_5 and 10 grams of carbon fiber were mixed in ethyl alcohol (C_2H_5OH) then heated from room temperature to 85°C, and soaked at this temperature for two hours. The system used for chemical treatment is shown in Figure 3.4.

Figure 3.4 : Picture of the Chemical Activation System

After chemical treatment, carbon fibers were washed with distilled water for five times to remove residual chemical solution. The washed carbon fibers were dried in air atmosphere for one day, and then they were put into a vacuum oven (Figure 3.5) at 50°C first day, 100°C second day, and 180°C third day.

Figure 3.5 : Picture of Vacuum Oven

Same process was applied with the chemical treatment of H_3PO_4 and HNO_3 for the chemical activation of carbon fibers. The picture of chemical treated carbon fiber is given in Figure 3.6.

Figure 3.6 : Chemical Treated Carbon Fiber

After this stages both of the chemical treated and untreated carbon fibers were carbonized and physically activated.

Stabilized carbon fibers were carbonized in nitrogen atmosphere at a flow rate of 20 ml/min. with different temperatures. Vertical furnace was used both carbonization and activation processes (Figure 3.7).

Figure 3.7 : Picture of Vertical Furnace

The carbon fibers were heated from room temperature to 600°C with a heating rate of 5°C/min. in nitrogen atmosphere. They were soaked 30 minutes at this temperature. At the second step, furnace was heated up to 900°C with a heating rate of 5°C/min. At this temperature the gas was switched to CO_2, and soaked for one hour. Then, the gas was switched again to nitrogen, and furnace was cooled down to the room temperature overnight.

Summary of carbonization and activation processes is given in Figure 3.8. The pictures of carbonized and activated carbon fibers are presented in Figure 3.9.

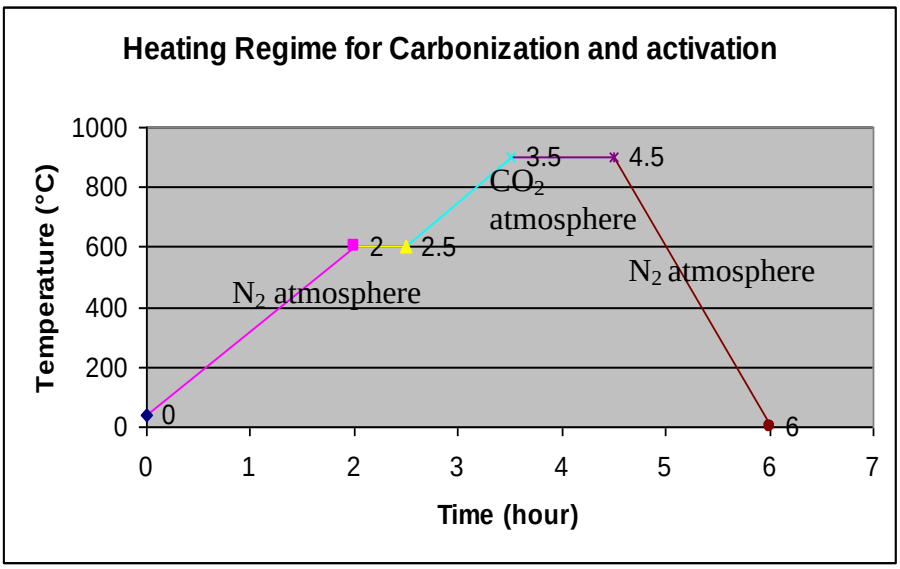


Figure 3.8 : Schematic Representation of Activation Process

Figure 3.9 : Activated Carbon Fiber

Some experiments were conducted in order to find optimum burn off time and temperature. For this purpose 10, 30, 60 and 120 minutes, and 700, 800, 900 and 1000°C were investigated under CO_2 atmosphere.

After optimization process, activation was carried out in three steps. In the first step, the carbon fibers were heated from room temperature to 350°C with a heating rate of 3°C/min in nitrogen atmosphere, and soaked 30 minutes at this temperature. In the second step, furnace was heated to 500°C with a heating rate of 2.5°C/min, and a soaking time of 30 minutes was applied. Furthermore, the fiber was also heated to 750°C with a heating rate of 2°C/minute. At 750°C the gas was switched to CO_2+Steam gas mixture for one hour. Finally, the gas mixture was switched again with nitrogen, and the furnace was cooled down to the room temperature overnight.

The activation procedure summarized above represents a slow heating regime at 750°C. Summary of activation process of slow heating regime at 750°C is given in Figure 3.10.

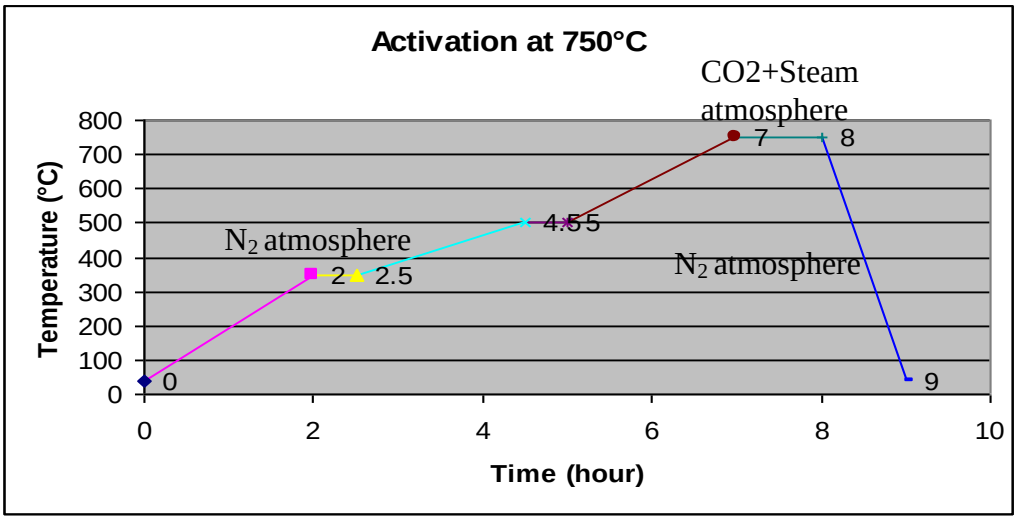


Figure 3.10 : Summary of Activation process of Slow Heating regime at 750°C

The experiment is repeated for a higher heating regime at 850°C as shown in Table Figure 3.11.

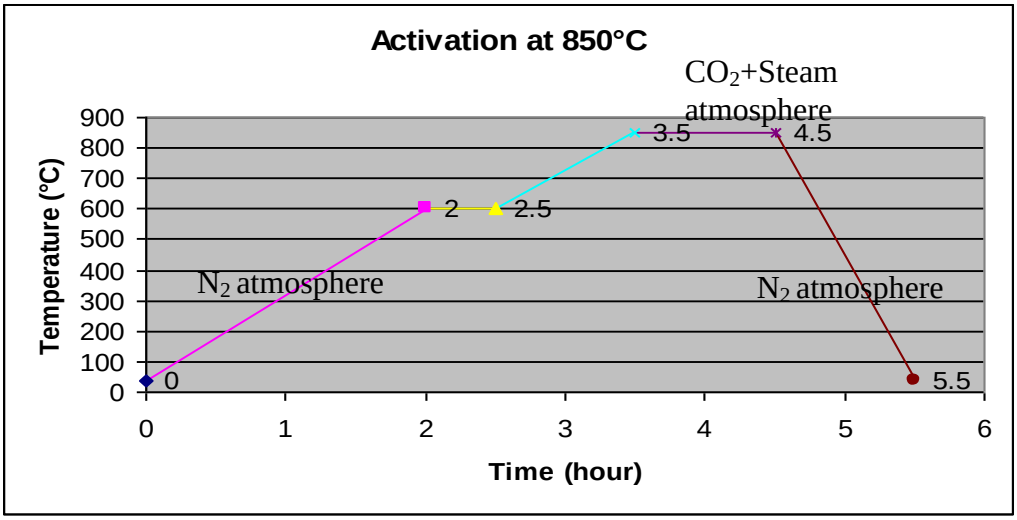


Figure 3.11 : Summary of Activation Process of Slow Heating Regime at 850°

3.3. Parameters for The Activation of Carbon Fibers

In this section the details of the selected parameters for the activation processes of carbon fibers are explained.

3.3.1. Temperature and Time and Burn-off Relationships

In order to find suitable temperature and time for the activation of carbon fibers two sets of experiments were carried out. In the first set of experiment, CO_2 activation was applied for 30 minutes at 700, 800, 900, and 1000°C. In the second set of experiments 10, 30, 60 and 120 minutes were applied under CO_2 atmosphere at 900°C. The appropriate temperature and time are determined using the % burn off of activated carbon fiber.

3.3.2. Gas Effect on the Activation Process of Carbon Fibers

For this set of experiments carbon fibers were treated with CO_2, steam and CO_2+steam mixture for physical activation at 900°C for 1 hour.

3.3.3. Temperature Effect on the Activation of Carbon Fibers

After the determination of most effective gas, three different temperatures, 750°C, 850°C, and 900°C were investigated to determine the effect of temperature on the activation of carbon fibers.

3.3.4. Effect of Chemical Treatment on the Activation of Carbon Fibers

After the selection of best performing gas, and temperature, the carbon fiber samples were treated with H_2SO_4, HNO_3, and H_3PO_4 to investigate the effect of chemical treatment on the activation of carbon fibers.

3.4. Characterization of Activated Carbon Fibers

Activated carbon fibers were characterized using surface area and pore size analyzer, TGA (Thermogravimetric Analyzer), Elemental Analyzer, SEM (Scanning Electron Microscope), and FTIR (Fourier Transform Infrared Spectroscopy).The details of the instruments and characterization procedures are given below.

3.4.1. Surface Area and Pore Size Analyzer

Surface area and porosity are two important physical properties for catalysts, adsorbents, medicines, rocks, and so on. Differences in the surface area and porosity of particles within a material can greatly influence its performance characteristics [50]. Physical and chemical gas adsorptions are the most widely used techniques to characterize surface area and porosity [38].

In physical gas adsorption an inert gas as nitrogen (or argon, krypton, carbon dioxide) is adsorbed on a solid material. Prior to the measurement the sample is pretreated at elevated temperature in vacuum or flowing gas to remove any contaminants [51]. Physisorbed molecules are fairly free to move around the surface of the sample. As more gas molecules are introduced into the system, the adsorbate molecules tend to form a thin layer that covers the entire adsorbent surface. Based on the well-known Brunauer, Emmett and Teller (B.E.T.) theory, one can estimate the number of molecules required to cover the adsorbent surface with a monolayer of adsorbed molecules, N_m. Multiplying N_m by the cross-sectional area of an adsorbate molecule yields the sample's surface area [36][38].

Continued addition of gas molecules beyond monolayer formation leads to the gradual stacking of multiple layers (or multilayers) on top of each other.

As the equilibrium adsorbate pressures approach saturation, the pores become completely filled with adsorbate. Knowing the density of the adsorbate, one can calculate the volume it occupies and, consequently, the total pore volume of the sample. If at this stage one reverses the adsorption process by withdrawing known amount of gas from the system in steps, one can also generate desorption isotherms. Adsorption and desorption isotherms rarely overlay each other. The resulting hysteresis leads to isotherm shapes that can be mechanistically related to those expected form particular pore shapes [38].

In this study surface area and pore size analysis are carried out using two equipments. Firstly, ASAP 2010 (Figure 3.12-a) is used for argon, nitrogen isotherms. Secondly AUTOSORB1 (Figure 3.12-b) is used for hydrogen isotherms.

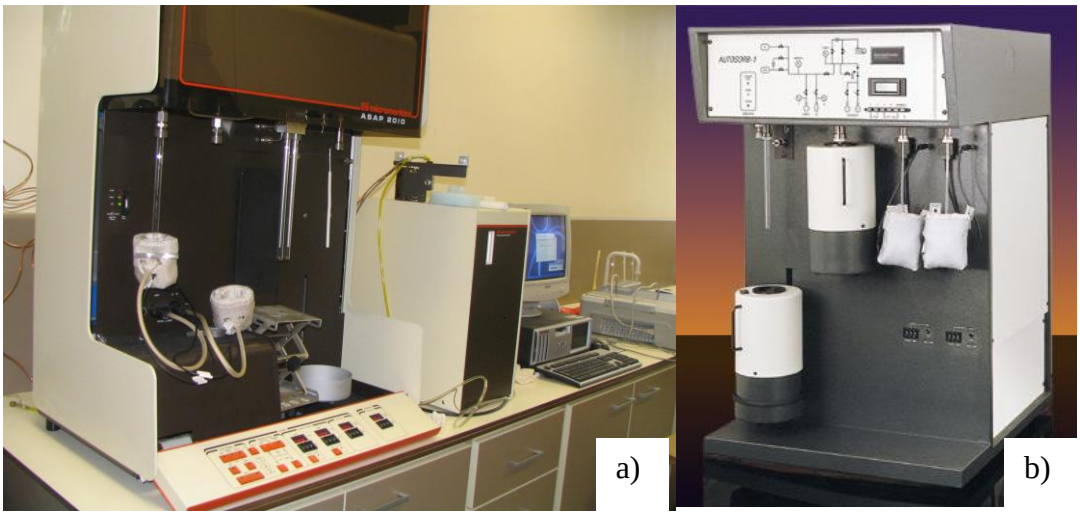


Figure 3.12 : Surface Area and Pore Size Analyzers a-) ASAP 2010, b-) AUTOSORB1

3.4.2. Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) is a technique used to measure changes in the weight (mass) of a sample as a function of temperature and/or time. The samples are heated or cooled at some selected rates which change between 5-20°C/min and also the temperature is maintained at a pre-selected value to be understood the changes by time [52].

With slow heating rate the neighboring peak can resolve. The loss in weight over specific temperature ranges provides an indication of the composition of the sample, including volatiles and inert filler, as well as indications of thermal stability. The inert (usually nitrogen and argon) and oxidative gas flow rates provide the appropriate environments for the test, and also CO_2 and steam can be used to understand activation yield .

A sample is placed into a TGA sample pan attached to a sensitive microbalance assembly. The sample holder portion of the TGA balance assembly is subsequently placed into a high temperature furnace. The balance assembly measures the initial sample weight at room temperature and then continuously monitors changes in sample weight (losses or gains) as heat is applied to the sample [51].

Thermo gravimetric analysis is used for different chemical investigations. Some of these are given below:

1. Thermal decomposition of inorganic, organic, and polymeric substances
2. Distillation and evaporation of liquids
3. Pyrolysis of coal, petroleum, and wood
4. Determination of moisture , volatiles, and ash contents
5. Thermal oxidative degradation of polymeric substance
6. Reaction kinetics studies
7. Thermal stability [14]

The thermo gravimetric analysis may be used for carbon fiber characterization especially for carbon composites [14]. Some typical thermogravimetric curves are shown Figure 3.13 [53]

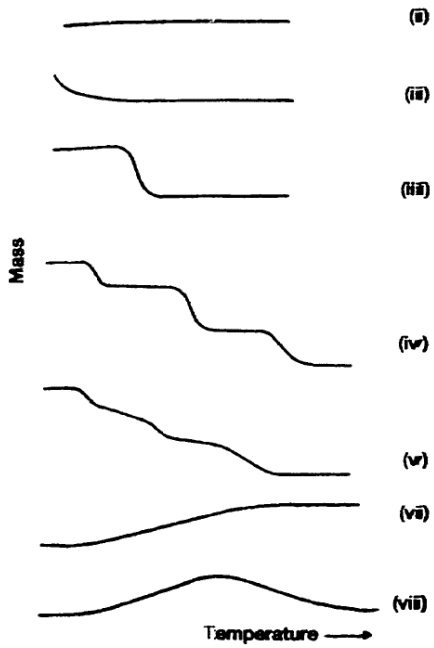


Figure 3.13 : Thermogravimetric Curves [51] [53]

The curves in Figure 3.13 can be explained that:

Type (i)curves are example for no decomposition

Type (ii) curves are for initial mass loss with generally desorption or drying.

Type (iii) curves are for one stage decomposition.

Type (iv) curves are for multistage decomposition with relatively stable intermediates.

Type (v) curves are also multi stage decomposition with nonstable intermediates.

Type (vi) curves show mass gain with a result of reaction of the sample with surrounding atmosphere.

Type (vi) curves are rare which are for the products of oxidation decomposition at higher temperature [53].

In this study Thermo gravimetric analysis is carried out using a SETARAM 92-16.18 which is displayed in Figure 3.14.

Figure 3.14 : Thermogravimetric analyzer (SETARAM 92-16.18)

3.4.3. Elemental Analysis

Elemental analysis gives the amount of elements in investigated sample. A small sample of compound especially 1-2 milligrams is burned in a pure oxygen atmosphere and the amount of carbon dioxide and water determines the percent composition of carbon and hydrogen in the sample. Another name of this analysis is combustion analysis [54]. In some of the available instruments there is no direct method to determine the amount of oxygen in a sample; this is usually done by subtracting the percent compositions of all other elements from 100%.

There are many different experiments for determining elemental composition. The most common type of elemental analysis is for carbon, hydrogen, and nitrogen (CHN analysis). This type of analysis is especially useful for organic compounds (compounds containing carbon-carbon bonds).

The elemental analysis of a compound is particularly useful in determining the empirical formula compound that contains the smallest set integer ratios for the elements in the compound that gives the correct elemental composition by mass of the compound [55]

In this study elemental analysis are carried out by using Carlo Erba 1106 (Figure 3.15).

Figure 3.15: Elemental analyzer (Carlo Erba 1106) [56]

3.4.4. Scanning Electron Microscopy (SEM)

Electron Microscopes are scientific instruments using a beam of highly energetic electrons rather than light to analyze object. By scanning an electron probe across a specimen, high resolution images of the morphology or topography of a specimen, with great depth of field, at very low or very high magnifications can be obtained [59]

A beam of electrons is produced at the top of the microscope by heating of a metallic filament. The electron beam follows a vertical path through the column of the microscope. It makes its way through electromagnetic lenses which focus and direct the beam down towards the sample. Once it hits the sample, other electrons (backscattered or secondary) are ejected from the sample. Detectors collect the secondary or backscattered electrons, and convert them to a signal that is sent to a viewing screen (Figure 3.16) [57].

In this study SEM analysis are carried out JEOL JSM-840 Scanning Electron Microscope (Figure 3.16).

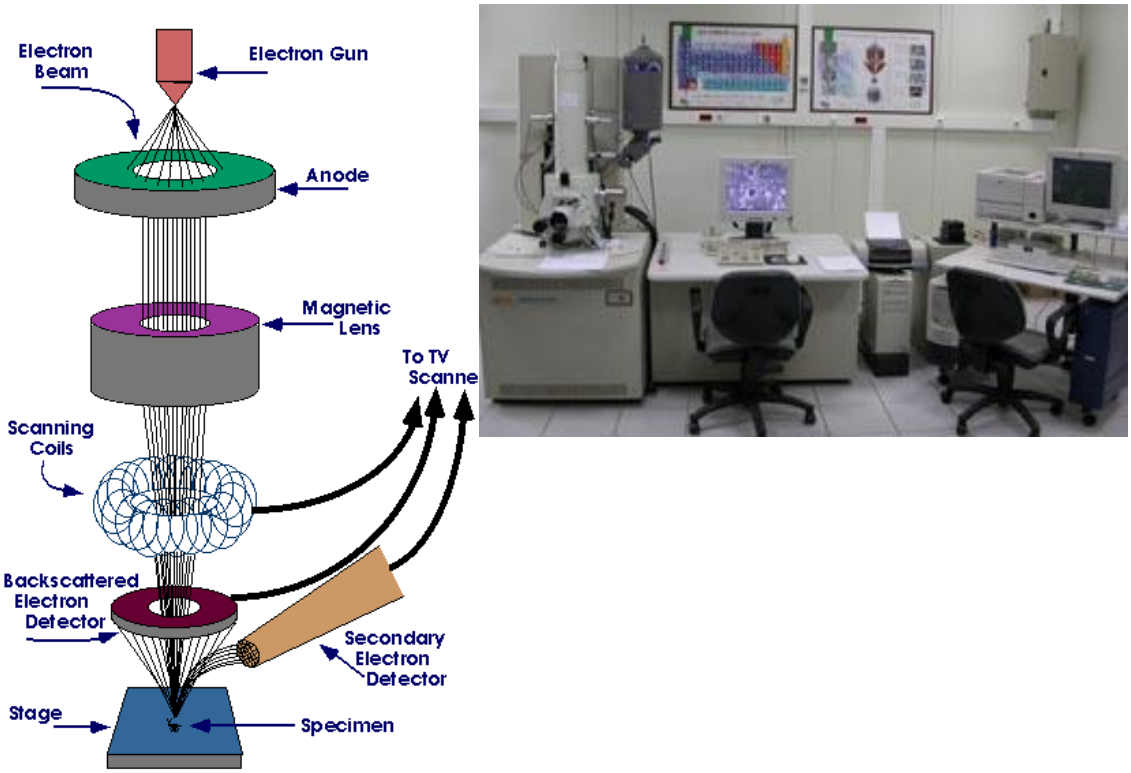


Figure 3.16 : Scanning Electron Microscope [58], [59]

3.4.5. Infrared Analysis (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is an analytical technique used to identify organics containing carbon compounds, including plastics, rubbers, and most lubricants. It can be utilized to analyze some components of an unknown mixture quantitatively; and can be applied to the analysis of solids, liquids, and gasses [60].

Depending on the elements and the type of bonds, molecular bonds vibrate at various frequencies. There are several specific frequencies which can vibrate for any given bond. Absorption bands in the range of 4000 - 1500 wave numbers are typically due to functional groups (e.g. -OH, C=O, N-H, CH_3, etc.). The region between 1500 - 400 wave numbers is referred to as the fingerprint region. Absorption bands in this region are generally due to intra-molecular phenomena, and are highly specific for each material. The specificity of these bands allows computerized data searches to be performed against reference libraries to identify a material [61].

In order to prepare sample for FTIR analysis some variant ways of changing the physical forms of samples are used. For instance, solid samples can be milled with

potassium bromide (KBr) to form a very fine powder. This powder is then compressed into a thin pellet which can be analyzed. KBr is transparent in the IR spectrum which provides this opportunity. Alternatively, solid samples can be dissolved in a solvent such as methylene chloride, and the solution placed onto a single salt plate. The solvent is then evaporated off, leaving a thin film of the original material on the plate. Solid samples can be measured directly measured in the recently developed IR spectrometers [61].

In this study FTIR analysis are carried out by Pelkin Ermer spectrum one (Figure 3.17)

Figure 3.17 : FTIR Analyzer

4. RESULTS AND DISCUSSION

Experimental results are given in this part of the study. The behaviors of the produced activated carbon fibers are investigated by evaluation of the experimental results with respect to the parameters involved and further using the characterization results. The parameters, which were used for the production of different activated carbon fibers, are pre-washing, burn-off relationships with time and temperature, gas, temperature, and chemical treatment.

Activated carbon fibers produced with this technique were examined with surface area and pore size analysis, TGA, elemental analysis, SEM, and FTIR. The results of all experiments and discussions on these results are presented below.

4.1.The Effect of Pre-washing on Activation of Carbon Fibers

In order to determine whether the carbon fibers had wax layer or not, they were washed with ethanol and methanol in soxhlet system. The washed samples are analyzed using TGA instrument. The TGA results of untreated carbon fiber and methanol and, ethanol washed carbon fibers are shown in Figure 4.1, Figure 4.2, and Figure 4.3 respectively.

TGA measurements are obtained using 30 mg samples from room temperature to 1100 °C with 10 °C /min heating rate under nitrogen atmosphere.

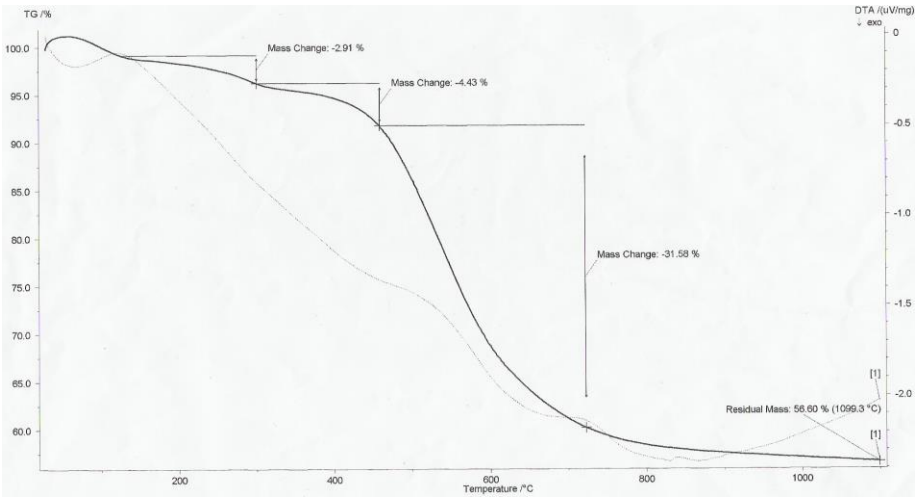


Figure 4.1 : Thermogravimetric Analysis of Carbon Fiber

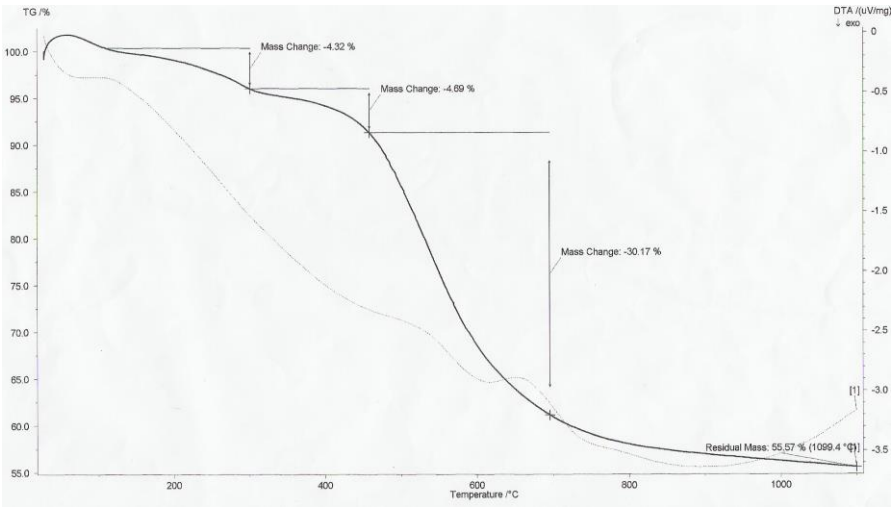


Figure 4.2 : Thermogravimetric Analysis of Methanol Washed Carbon Fiber

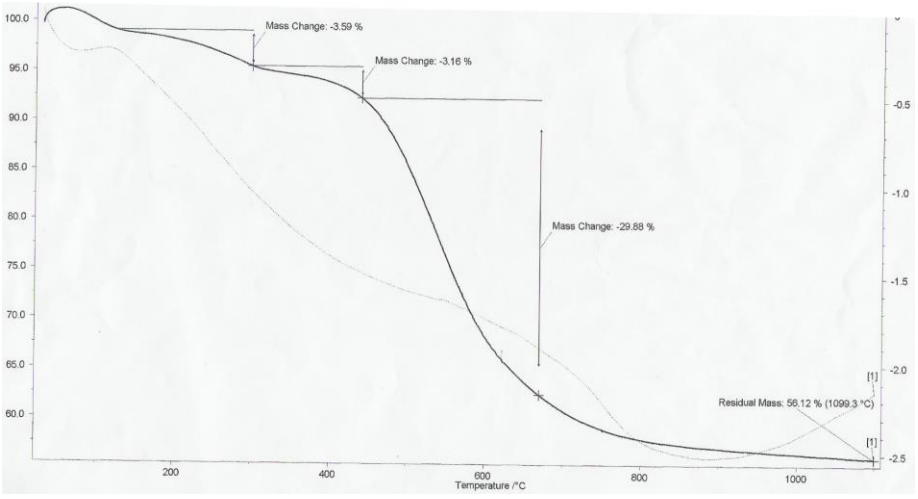


Figure 4.3 : Thermogravimetric Analysis of Ethanol Washed Carbon Fiber

The summary of TGA studies for pre-washing is given Table 4.1 It is apparent from the Table 4.1 that all of three samples give almost similar carbon yields as obtained from TGA results. Therefore, pre-washing step is found unnecessary, and eliminated from the experimental procedures.

Table 4.1 : Summary of TGA Studies for Pre-washing

Samples	Carbon yield (%) 1100 ° C
Carbon fiber	56.60
Ethanol Washed Carbon Fiber	56.12
Methanol Washed Carbon Fiber	55.57

4.2. Effect of Temperature and Time on Burn-off

The results for burn off of activated carbon fibers obtained at four different temperatures are compiled figure 4.4.

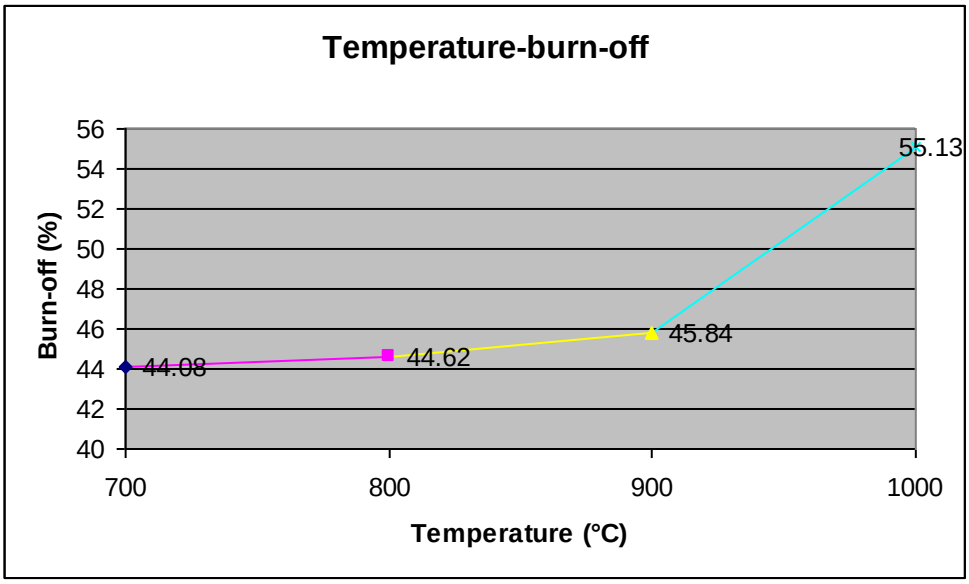


Figure 4.4 : Burn-off of Carbon Fibers with Temperature

As it is observed from Figure 4.4, burn-off increases slightly with increasing temperature in CO_2 activation up to 900°C. After 900°C, burn-off increases rapidly, related to the rapid decrease in the yield of activated carbon fiber after 900°C.

Burn-off of activated carbon fibers obtained at four different times is compiled in Figure 4.5.

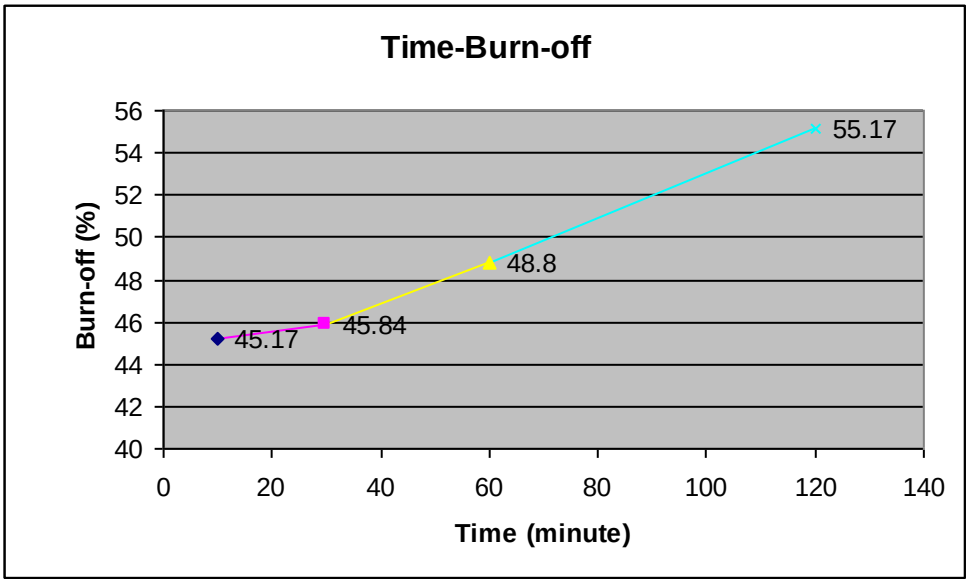


Figure 4.5 : Burn-off of Carbon Fibers with Time

As it is obvious from Figure 4.5, burn-off increases slightly with increasing activation time in CO_2 up to 30 minutes. After 30 minutes, while burn-off rises rapidly, the yield decreases. This phenomenon is expected because as the temperature rise more volatilization occurs, resulting the decrease in the yield of the samples. The reaction is reversible and endothermic as temperature increase the reaction rate increase also the reaction shift towards products.

4.3. Effect of Gas Atmosphere on the Activation of Carbon Fibers

For this set of physical activation experiments carbon fibers are activated with CO_2, steam and the mixture of CO_2+ steam at 900 °C for one hour.

Table 4.2 displays burn off of activated carbon fibers with activation gases. It is observed that the burn-off is the highest for CO_2+ steam activation. It is known that as series of reaction occur during the steam activation some of products of steam reactions also react with carbon fibers which increase the burn off of the samples. These results are consistent with the data reported in literature [62].

Table 4.2 : Burn-off Change with Activation gases

Gas	Burn off (%) (900 °C, 1 hour)
CO_2	48.8
Steam	75
CO_2+ Steam	87

Seung-Kon Ryu [62] studied the yield of activated carbon fiber during carbonization and activation of phenolic resin based fiber. There, it was reported that the increase of the burn-off was not influenced much by the type of activation gases up to 700°C. However, above the 700°C the effect of gas atmosphere was found to be substantial especially for the steam-nitrogen gas mixture. Figure 4.6 shows the yield of phenolic resin based activated carbon fiber determined by thermogravimetry, as a function of temperature.

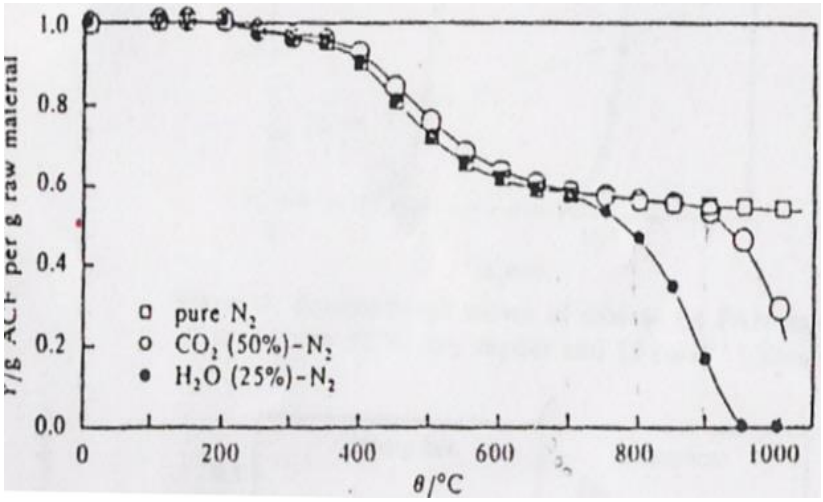


Figure 4.6 : Yield of Phenolic Resin Based Activated Carbon Fiber [62]

In an other study, Ryu and coworkers [63] reported substantial amount of on weight loss as a function of time, activation gas and temperature. As can be seen Figure 4.7 the burn off of the steam activation is more rapid than burn-off of the CO_2 activation at 900°C. The activation temperature is also found to be an important parameter for activation gases. If the temperature of CO_2 activation is increased from 900°C to 1000°C the weight loss was much steeper as they showed in Figure 4.7.

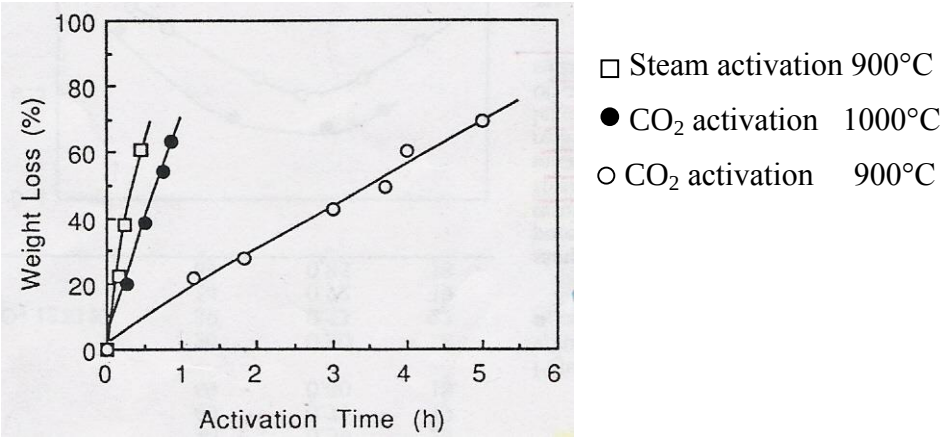
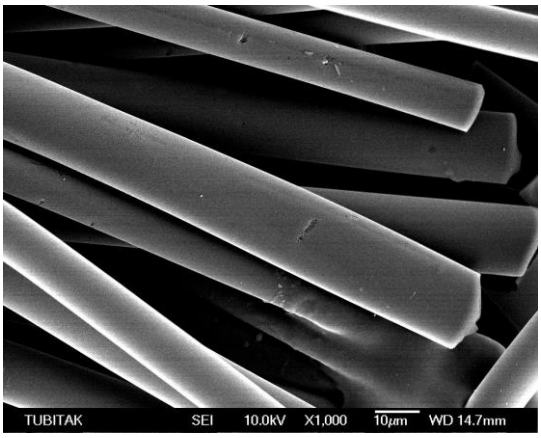


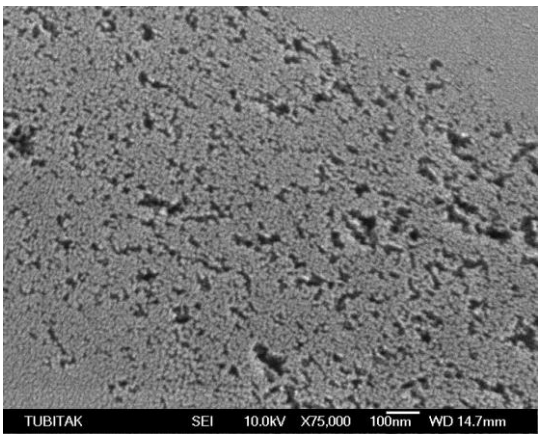
Figure 4.7: Burn-off of Pitch Based Activated Carbon Fiber [63]

After this set of experiments, because of the high weight loss, the heating regime of activation reevaluated and changed in order to decrease burn off as reported in section 3.2. The new heating regime is applied for the other sets of experiments.

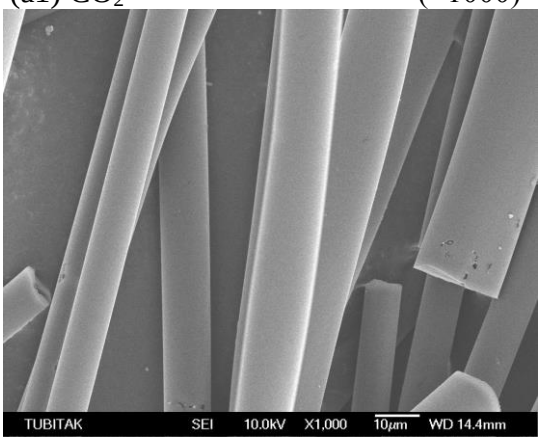
The surface morphology of resulting activated carbon fibers are examined with SEM. The SEM images are obtained with 1000 and 50000 magnifications to observe gas effect on the activation process of carbon fibers (Figure 4.8).



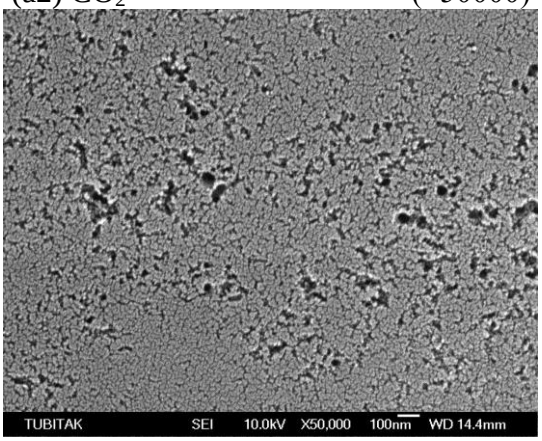
(a1) CO_2 (×1000)



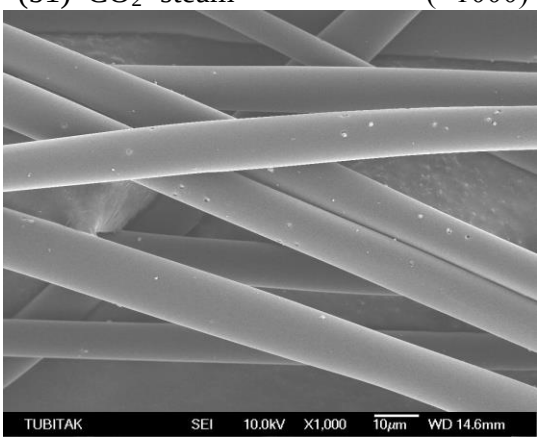
(a2) CO_2 (×50000)



(b1) CO_2+steam (×1000)



(b2) CO_2+steam (×50000)



(c1) Steam (×1000)

Figure 4.8 : SEM Micrographs of Gas Effect on the Activation Process of Carbon Fibers at 900°C

From Figure 4.8, it was not possible to observe the porous structure of activated carbon fibers, at 1000 magnification due to insufficient magnification. The porosity can be observed from 50000 magnifications. However, even at this magnification, only the pores that are larger than 50 nm can be observed. In other words, only macropores can be clearly identified from SEM images.

White spots observed on the surface of the fibers as can be seen from Figure 4.8-c1, are thought to be macropores. However, magnification to 50000 is not proved this thought. Therefore, energy dispersive spectrometer (EDS) analysis was conducted to identify these spots. The analysis revealed that these white spots were due to surface impositions due to the copper impurities that are torn from carbonization furnace.

The SEM studies of phenolic based activated carbon fibers are rarely reported in literature. Economy and coworkers [64] examined phenolic based activated carbon fibers with SEM. Their results are in close agreement with the present study (Figure 4.9).

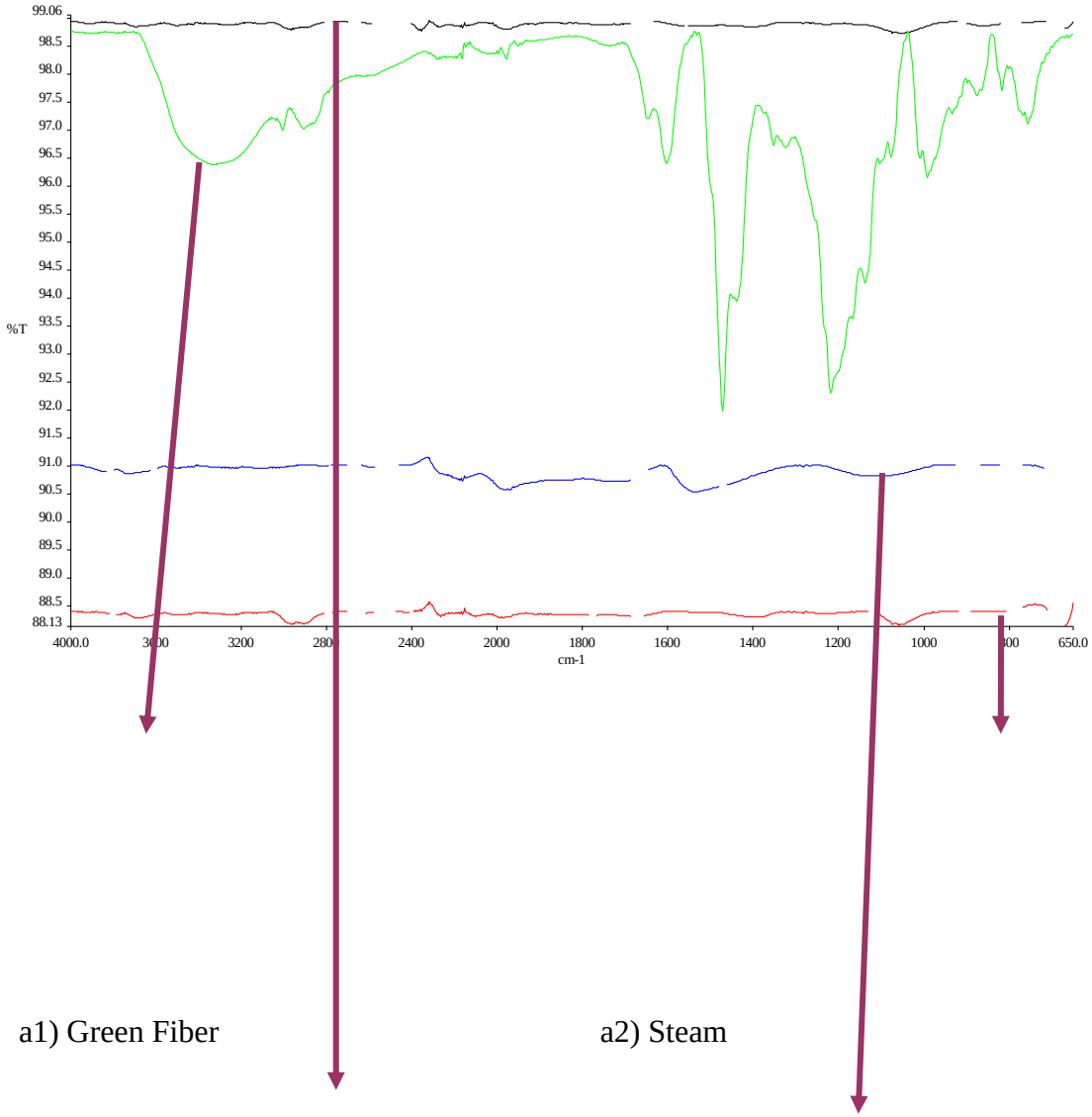
Figure 4.9: SEM Micrograph of Phenolic Based Activated Carbon Fiber [64]

The elemental analysis results for carbon fibers which are activated with different gases are given in Table 4.3. The analysis shows that, the green fibers have the lowest carbon content while samples activated with CO_2+ Steam has the highest carbon content. Fibers activated with steam and CO_2 has the value of 82.26 and 89.14% carbon content respectively and like the increase in the burn-off, the carbon content of the activated carbon fibers increased from green fibers to steam, to CO_2, and to CO_2+ Steam gases. The elemental analysis change with burn off is also in close agreement with the results reported in literature [65].

Table 4.3: Elemental Analysis of the Carbon Fibers Activated with Different Gases

Gas	(900 °C, 1 hour)	
	% C	% O
Green fibers	65,57	28,13
Steam	82,26	17,73
CO_2	89,14	10,86
CO_2+ Steam	93,75	6,25

The activated carbon fibers are examined with FTIR in order to observe the functional groups on their structure. The FTIR spectra of the green carbon fiber is given Figure 4.10. The band at 990cm^{-1} is assigned to the olephinic groups. The band at 1216 cm^{-1} is assigned to C-O stretching and the band at 1470 cm^{-1} is assigned to the –CH groups. The band at 1600 cm^{-1} is assigned to the stretching of aromatic C=C groups and the band at 2968-2864 are due to the stretching of saturated hydrocarbons.. The FTIR spectrum of carbon fibers activated with various gases are also given in Figure 4.10. The investigation of the FTIR spectrum showed that all the gases and gas mixture has different spectrum with a small number of common groups such as in the band of 1000-1100 cm^{-1} and the band of 1950-2000cm^{-1}. While the peak appears for steam and CO_2 in he band of 2968-2864cm^{-1} the peak for is not appeared for the mixture of these two gases. This may due to the removal of saturated hydrocarbons. The results are also consistent with elemental analyses. The carbon content for the sample treated with the mixture of gases is less compared to the other samples treated with steam and CO_2 separately.

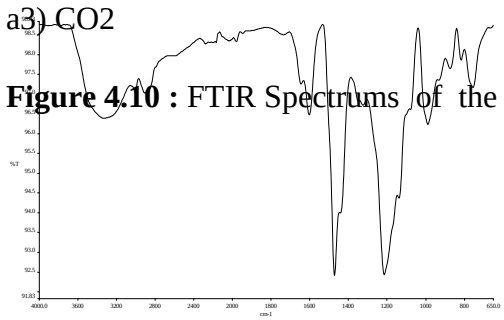


a1) Green Fiber

a2) Steam

a3) CO2

a4) CO2+steam



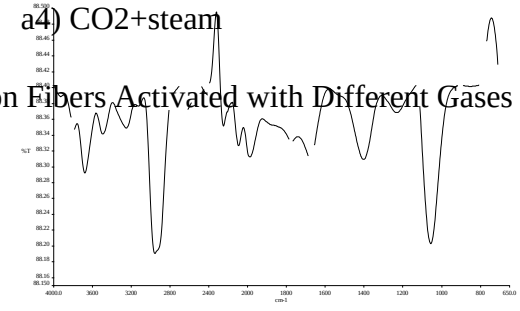


Figure 4.10 : FTIR Spectrums of the Carbon Fibers Activated with Different Gases

The BET surface area, external surface area, and micropore area for carbon fibers activated with different gases in nitrogen atmosphere are given in Table 4.4.

Table 4.4 : Surface Areas of Carbon Fibers Activated with Different Gases (in Nitrogen Atmosphere)

Type of gas (900 °C, 1 hour)	BET Surface area (m^2/g)	External Surface Area (m^2/g)	Micropore Area (m^2/g)
Steam	784	84	700
CO_2	1022	107	915
CO_2+ Steam	3076	890	2186

External surface area, non-microporous of part of the material, is calculated with V- t plot equation. The procedure is the same as that employed in the BET surface area measurement, but it extends the pressure range to higher pressures to permit calculation of the external surface area. Moreover, subtraction of the external surface area from BET s surface area gives the micropore area of the material [38].

As it is seen from Table 4.4, BET surface areas of samples are 784 m^2/g for steam activation, 1022 m^2/g for CO_2 activation, and 3076 m^2/g for CO_2+steam mixture activation. Furthermore, mixing of gases increases the surface area 3-4 times higher than the activation with steam and CO_2 separately. While CO_2 generates narrow pore size distribution, steam generates wider pore size distribution on activated materials (Section 2.4.3.1). When CO_2 +steam mixture is used in activation process, their combined effect results in a distinct synergy. The mechanism behind this behavior is not proven however the fact that the two gasses developing different types of pores working on top of each other is expected to cause this sharp increase.

Adsorption isotherms are key components for understanding of the surface area and porosity of materials. The amount of nitrogen adsorbed on activated carbon fiber is used to calculate specific surface area by means of BET equation. Usually nitrogen adsorption isotherms at 77K are used in literature.

The nitrogen isotherms for carbon fibers which are activated with different gases are given in Figure 4.11.

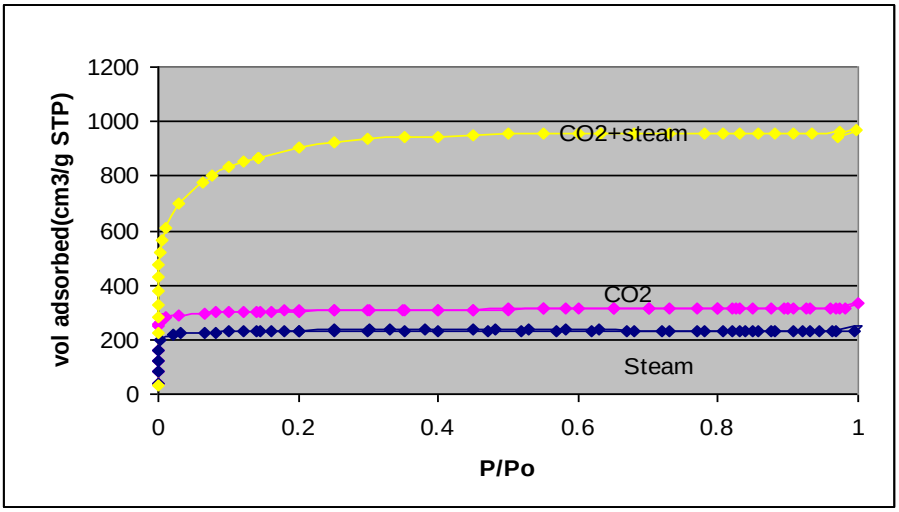


Figure 4.11: Nitrogen Isotherms for Carbon Fibers Activation with Different Gases

It is clear from the Figure 4.12 that all of the isotherms of carbon fibers activated with different gases are similar. According to the BET's classification (Section 2.6.3), they show type I isotherm. Type I physisorption isotherms are exhibited by microporous solids having relatively small external surface. However, when the isotherm of carbon fibers activated with CO_2+steam mixture is observed, it is slightly different than the isotherms of carbon fibers activated with CO_2 and steam. When the nitrogen isotherms of the samples are converted to semi-logarithmic scale of relative pressure (Figure 4.12), this difference can be observed better.

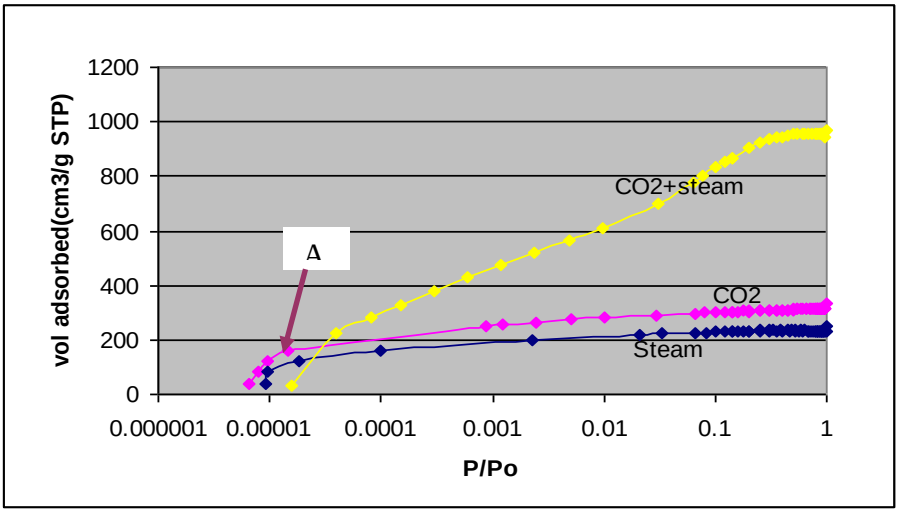


Figure 4.12 : Nitrogen Isotherms for Carbon Fibers Activation with Different Gases (Semi-logarithmic Scale)

In Figure 4.12, the knees of the CO_2 and steam activated carbon fiber isotherms about $P/Po<10^{-5}$ (A) are behaving such that after a sudden increase they show a slow increasing slope in nitrogen adsorption. However the volume absorbed responded at relatively higher P/Po (relative pressure) for the combined CO_2 and steam activation but the increase in volume absorbed with P/Po occurs with a much higher slope compared to the activation by each individual gases. In literature, it has been reported that for type I isotherms of carbon based materials at lower P/Po represents microfilling mechanism, and the slope at high relative pressure is the reason of multilayer adsorption and condensation on non-microporous materials like in mesopores, in macropores, and on the external surface [66].

In order to understand the influence of the physical activation of gases on the microporosity of activated carbon fibers, the pore size distribution is a key element. A number of methods were developed for pore size distribution analysis. A density functional theory method is one of them [38]. Classical macroscopic theories like the Dubinin Raduskevich approach do not give realistic description of the filling of micropores even narrow mesopores. Pore size distribution of density functional theory (DFT) gives much more accurate results for pore size analysis [38]. In this study, porosity distribution by original density functional theory is used (at 77K with nitrogen on carbon materials-slit pores model).

Incremental and cumulative pore volumes with pore width of steam activated carbon fibers are given in Figure 13-a, and Figure 13-b respectively.

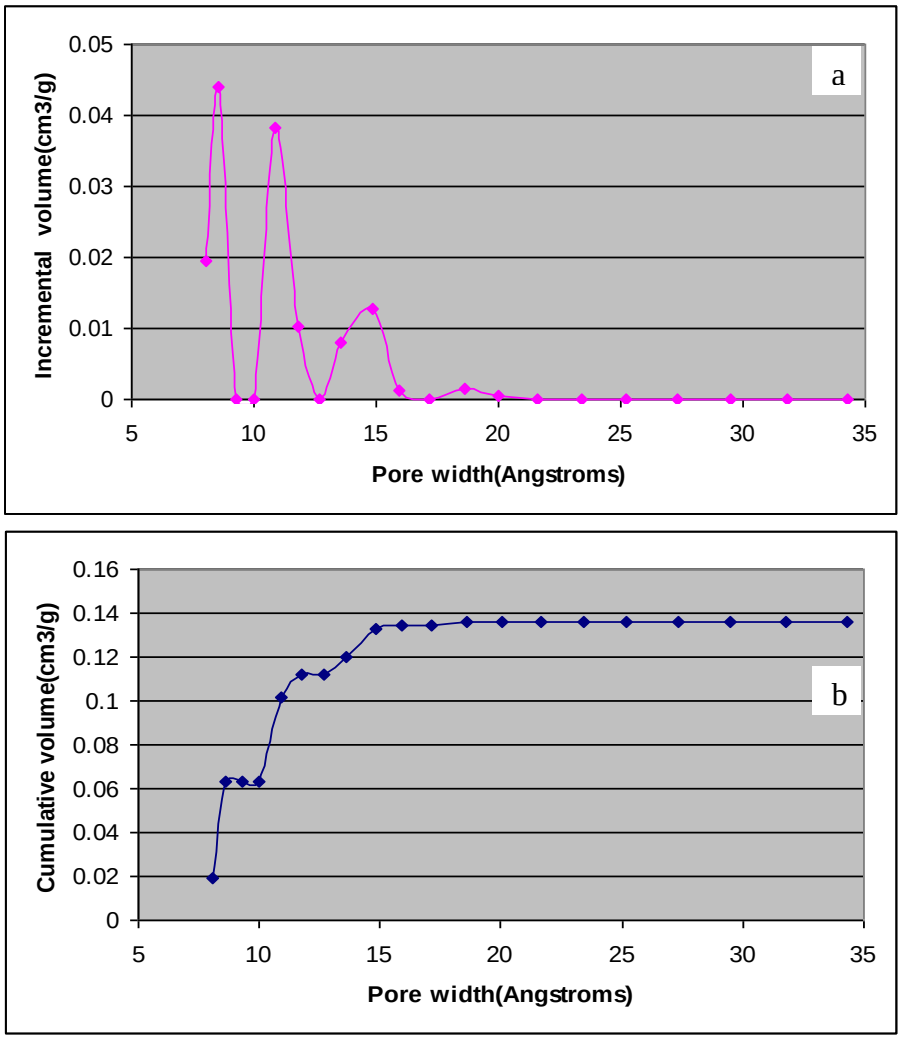


Figure 4.13 : Relationship between Incremental and Cumulative Pore Volumes with Pore Width of Carbon Fibers Activated with Steam

As it is seen from Figure13-a, and Figure 13-b that the sample has only micropores smaller 20 angstroms, most of them are supermicropores between 7-20 angstroms.

Incremental and cumulative pore volumes with pore width of CO_2 activated carbon fibers are given in Figure 15-a, and Figure 15-b respectively.

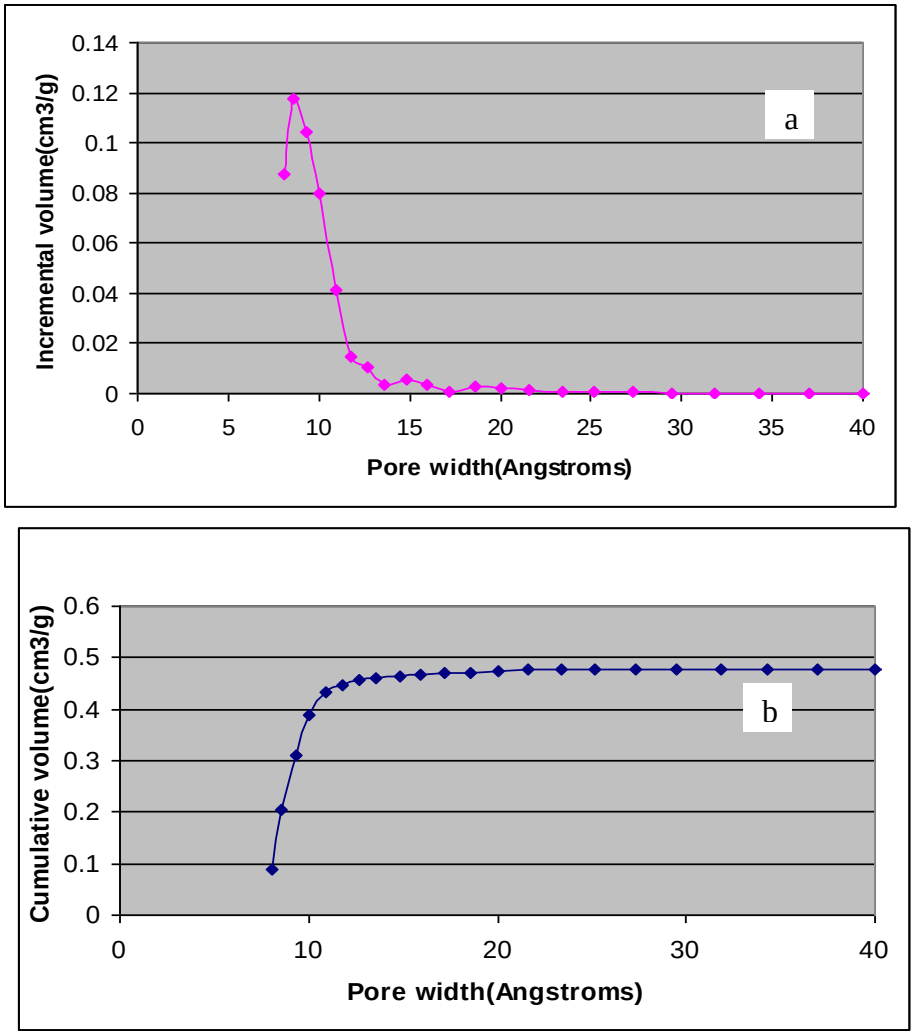


Figure 4.14 : Relationship between Incremental and Cumulative Pore Volumes with Pore Width of Carbon Fibers Activated with CO_2

The pore characterization of the samples shows dominant micropores and little mesopores and macropores.

Incremental and cumulative pore volumes with pore width of for carbon fibers activated with CO_2+steam gas mixtures are given in Figure 15-a and Figure 15-b .

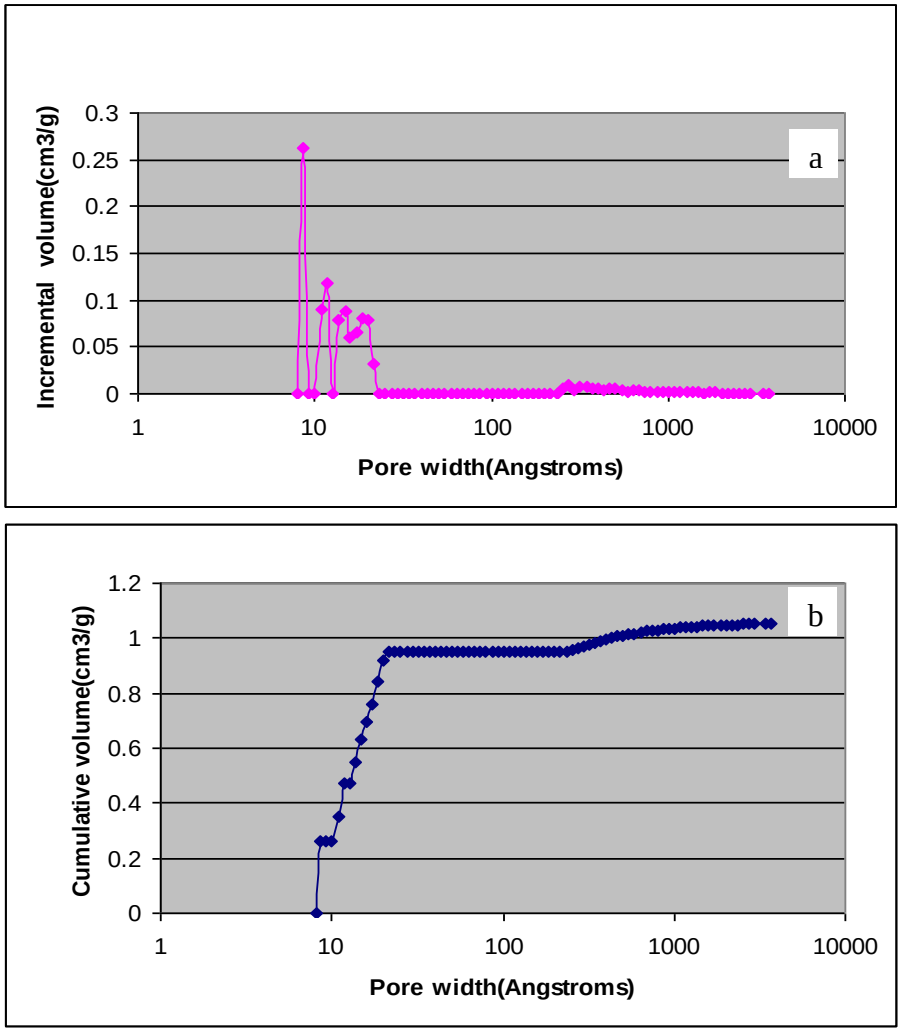


Figure 4.15 : Relationship between Incremental and Cumulative Pore Volumes with Pore Width of Carbon Fibers Activated with CO_2+Steam

The activated samples with CO_2 and steam together have much more micropores compared to the fibers activated by the two gases separately. Moreover, in gas mixture activation appreciable amount of mesopores and macropore volumes were observed.

The distribution of pore volume among micropores (<20 angstrom), mesopores (20<x<500 angstrom), and macropores (>500 angstrom) for different activation gases are also compiled in Figure 4.16.

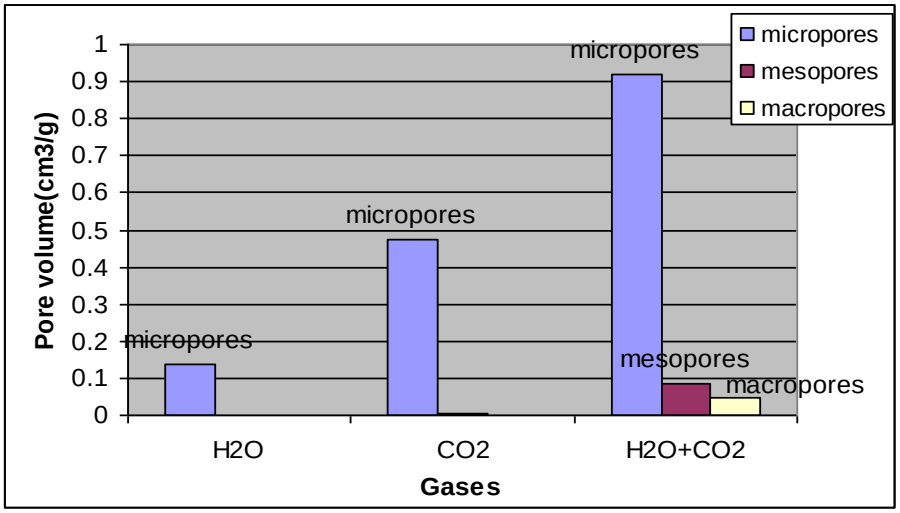


Figure 4.16 : The Distribution of Pore Volume with Micro, Meso, and Macropores for Carbon Fibers Activated with Different Gases

In Figure 4.16, the micropores are the dominant pores for all gas activations. Volumes of micropores are 0.14 cm^3/g for steam, and 0.47 cm^3/g for CO_2. Theoretically, if there is linear relationship between steam activation and CO2 activation, it may be expected that the total micropore volume of CO_2+steam activation be around 0.61 cm^3/g (0.14+0.47). However, the micropore volume for CO_2+steam activation is well higher than expected value (0.61 cm^3/g) and obtained as 0.92 cm^3/g. This is similar to the synergistic results observed for the surface area increase for the activation with mixture of two gases.

Traditionally, the adsorption isotherm analysis is made with nitrogen at 77K. At this temperature, diffusion of nitrogen molecules into carbon micropores is very slow. Moreover, the use Argon may be expected to provide more accurate pore size measurement because argon adsorption is almost not affected by any specific interactions with carbon surface groups [52]. Therefore, in this study, argon isotherms for carbon fibers activated with different gases (Figure 4.17 and Figure 4.18) are used beside nitrogen isotherms (for some samples) for comparison of the characterization of the micropores.

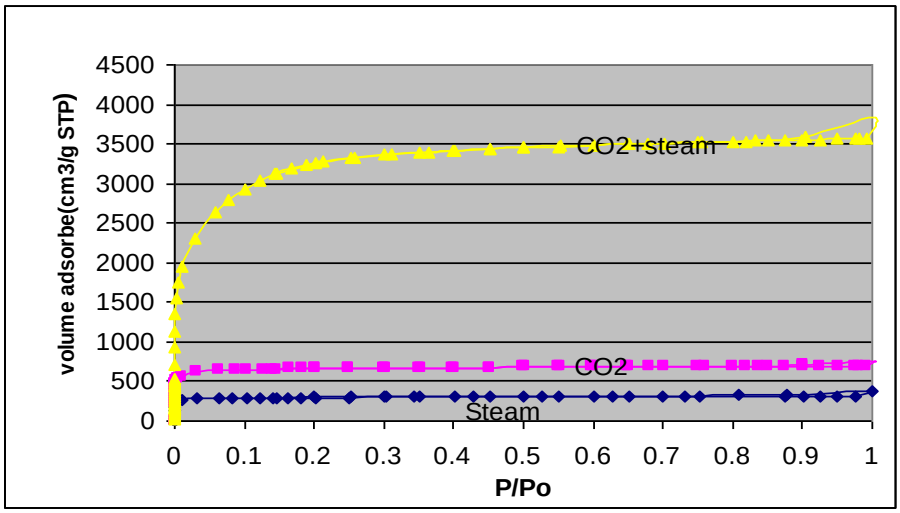


Figure 4.17 : Argon Isotherms for Carbon Fibers Activation with Different Gases

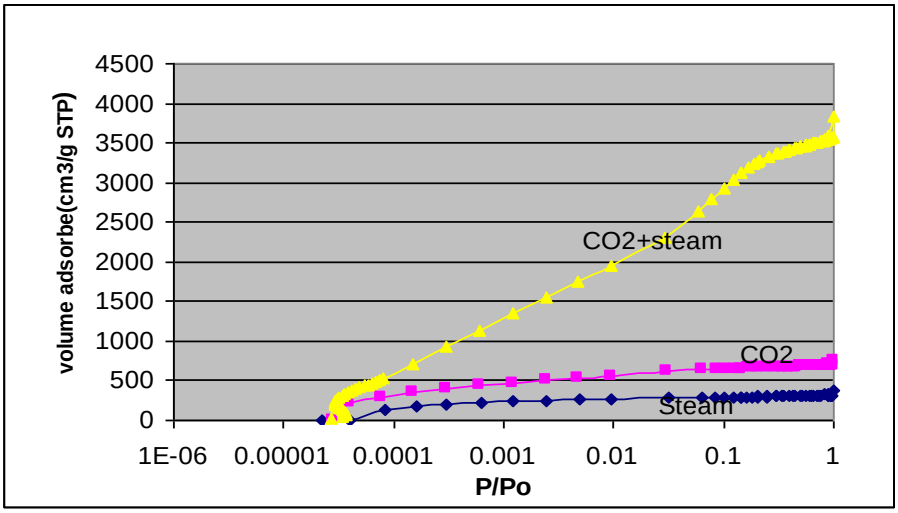


Figure 4.18 : Argon Isotherms for Carbon Fibers Activation with Different Gases (Semi-logarithmic Scale)

All of the argon isotherms of the activated carbon fibers have similar properties. According to the BET's classification, they have type I isotherm. However, when looked at the logarithmic scale isotherm, it becomes more apparent that for CO_2+steam mixture activation there is apparent differences compared to the other gas isotherms. Semi-logarithmic scale isotherm shows that the knees of the CO_2 activated and steam activated samples about $P/Po<10^{-4}$ are round, and the argon adsorption slightly increases with increasing P/Po ratio. However, CO_2+steam mixture activation isotherm shows a much sharper increase in Argon adsorption with P/Po ratio compared to CO_2 activated and steam activated samples.

The external surface area, micropore area, and BET surface area for carbon fibers activated with different gases in argon atmosphere are given in Figure 4.19.

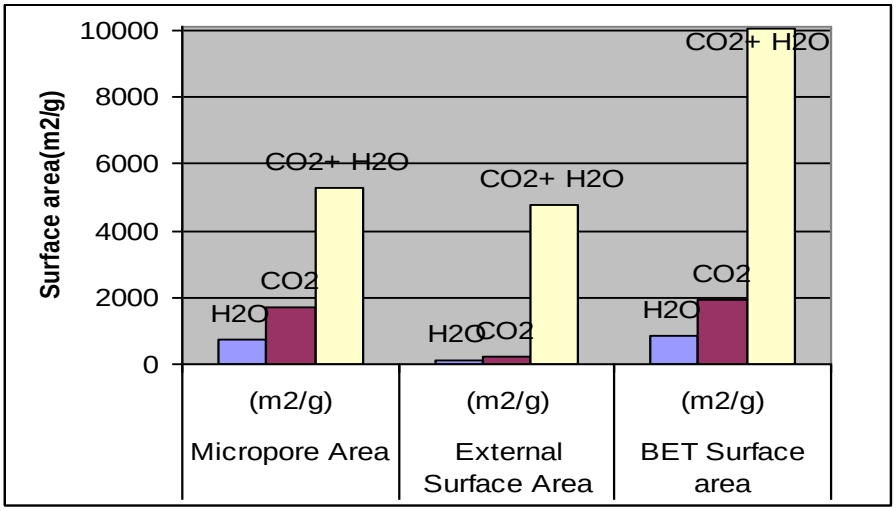


Figure 4.19 : Surface Areas of Carbon Fibers Activated with Different Gases in Argon Atmosphere

BET surface areas of samples are measured as 870 m^2/g for steam activation, 1934 m^2/g for CO_2 activation, and 10057 m^2/g for CO_2+steam mixture activation. The characteristics of the Argon BET surface areas show similar behavior as nitrogen measurements, but measured values of surface areas with argon are much higher compared with the values measured with nitrogen. The reason for the differences may be explained that argon is adsorbed to its equilibrium value much faster than nitrogen. This may explain in terms of their kinetic diameters which are reported to be 3.405 angstrom and 3.64 angstrom for Argon and Nitrogen, respectively.

4.4. The Effect of Temperature on the Activation of Carbon Fibers

For this set of experiments, carbon fibers are activated at three different temperatures with CO_2+steam gas mixture for 1 hour. The temperatures used in these experiments are 750°C, 850°C, and 900°C.

Table 4.5 presents burn off of activated carbon fibers at different temperatures. It can be seen from the Table 4.8 that the carbon yield decreases as the activation temperature increases. The burn-off ratio is nearly twice with increasing temperature from 750°C to 900°C. TGA results explained this behavior (Figure 4.6). The curve between 600-1000°C is critic temperature band for weight loss, and the weight loss increase is sharp around 800°C.

Table 4.5: Burn-off Change with Temperature

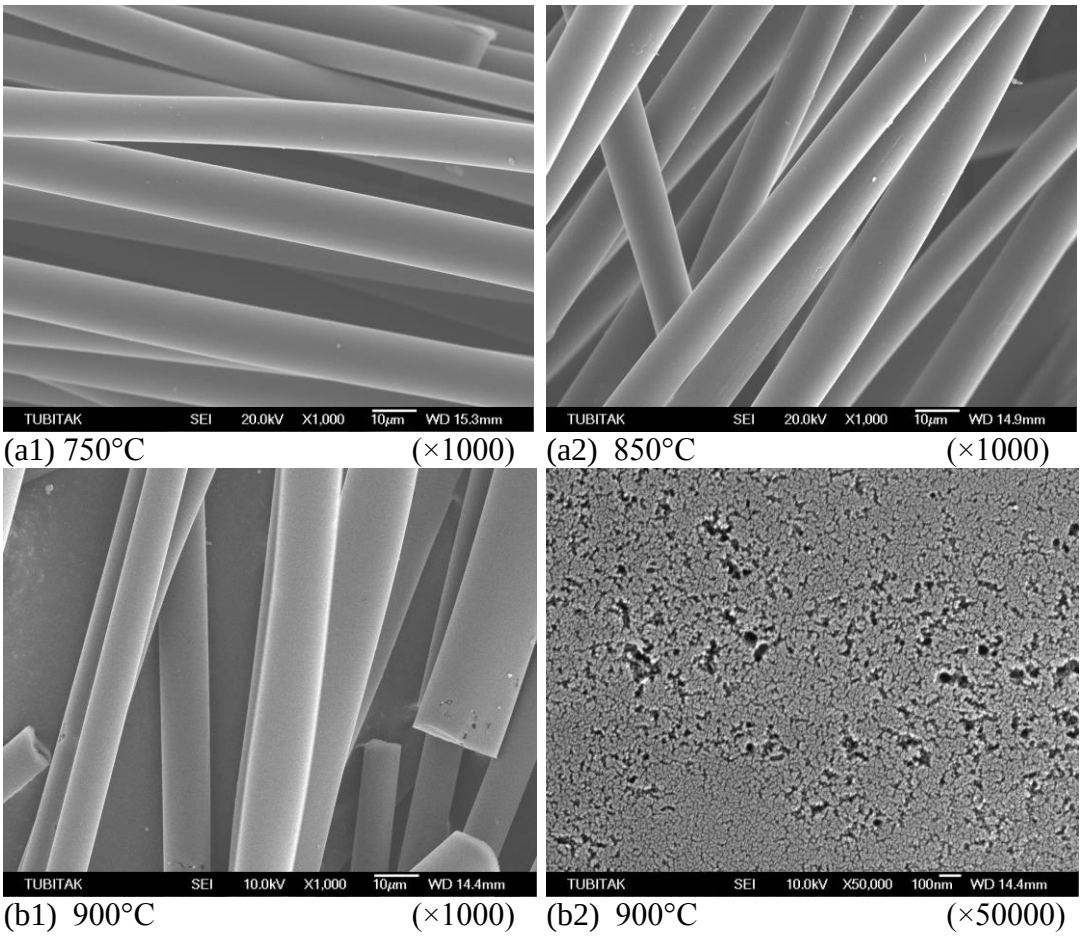
Temperature (°C)	Burn off (%) (CO_2+ Steam, 1 hour)
750	47
850	70
900	87

The elemental analysis results for carbon fibers which are activated at different temperatures are given in Table 4.6. As it is expected, the carbon contents of the activated carbon fibers increase with activation temperature. Carbon content increased from 87.67 (weight %) to 93.75, as the temperature increased from 750 to 900° C. This behavior is explained in terms of preferential devolatilisation with temperature increase.

Table 4.6: The Elemental Analysis of the Carbon Fibers Activated at Different Temperatures

Activation Temperature (°C)	(CO_2+Steam, 1 hour)	
	% C	% O
Green fiber	65,57	28,13
750	87.67	12.01
850	89.05	8.17
900	93,75	6,25

The SEM images obtained with 1000 and 50000 magnifications for activated carbon fibers at different temperatures are given in Figure 4.21.



(a1) 750°C (×1000) (a2) 850°C (×1000)

(b1) 900°C (×1000) (b2) 900°C (×50000)

Figure 4.20: SEM Micrographs of Carbon Fibers Activated Different Temperatures

The porosity is not observed for 1000, and 50000 magnification for SEM images at 750°C and 850°C. At these temperatures carbon fibers have microporosities which are smaller than 20 angstrom, therefore can not be observed from SEM images at the given magnifications. However at 900°C, it is possible to obtain macroporous structure, for this reason as shown in Figure 4.21(b2) the porosity is observed at 50000 magnifications.

FTIR spectrums for carbon fibers activated at different temperatures are given in Figure 4.22. The investigation of the FTIR spectrums showed that for various temperatures the samples have different spectrum with a small number of common peaks such as in the band of $1600cm^{-1}$ which is assigned to the stretching of aromatic C=C groups and the band $3050cm^{-1}$ to the stretching of aromatic groups. The peaks intensity at $3050cm^{-1}$ is increased as the temperature increased as a sing of aromaticity increase.

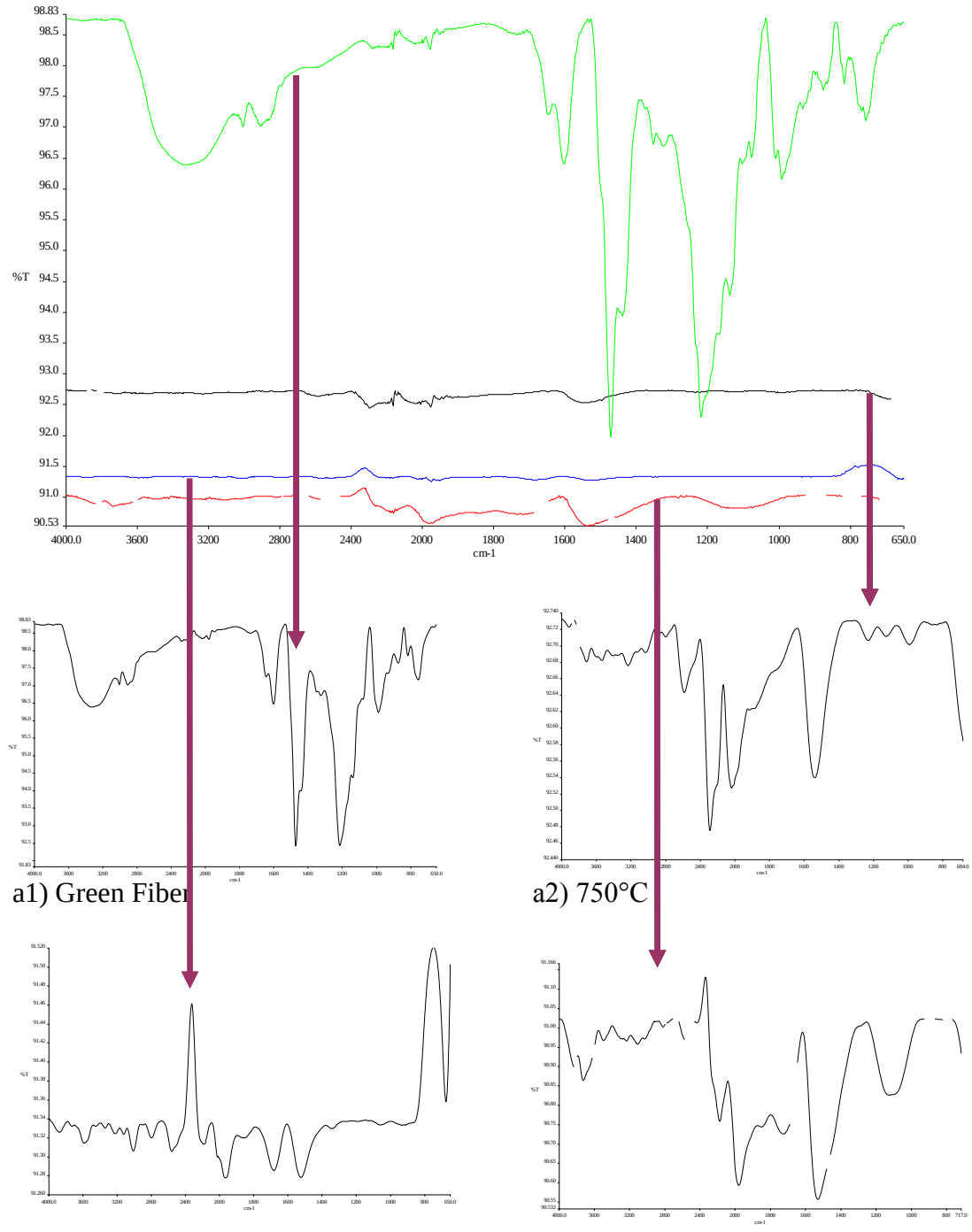


Figure 4.21 : FTIR Spectrums of Carbon Fibers Activated Different Temperatures

The BET surface area, external surface area, and micropore volume for carbon fibers activated at different temperatures are compiled in Figure 4.23.

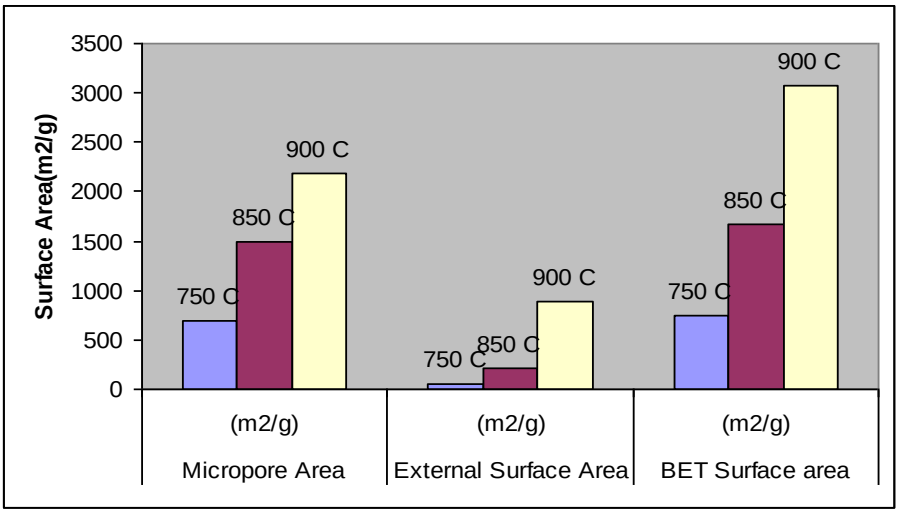


Figure 4.22: Surface Areas of Carbon Fibers Activated at Different Temperatures

As it is observed from Table 4.10 and Figure 4.22, BET surface areas of samples are 739, 1670, and 3076 m^2/g for 750°C, 850°C, and 900°C respectively. Increasing temperature increases the reaction rate, and the amount of devolatilisation increases resulting in increased surface area of the material.

The nitrogen isotherms for carbon fibers which activated at different temperatures are given in Figure 4.23, and Figure 4.24.

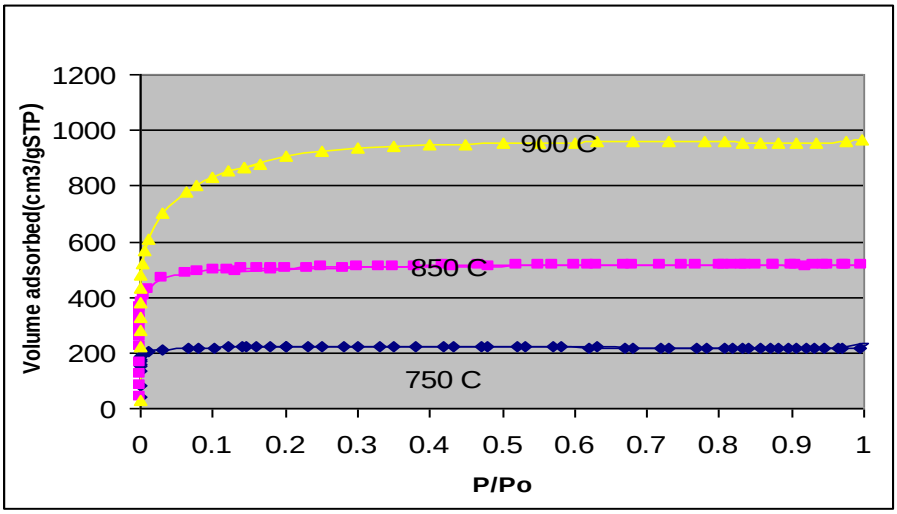


Figure 4.23: Nitrogen Isotherms for Carbon Fibers Activation at Different Temperatures

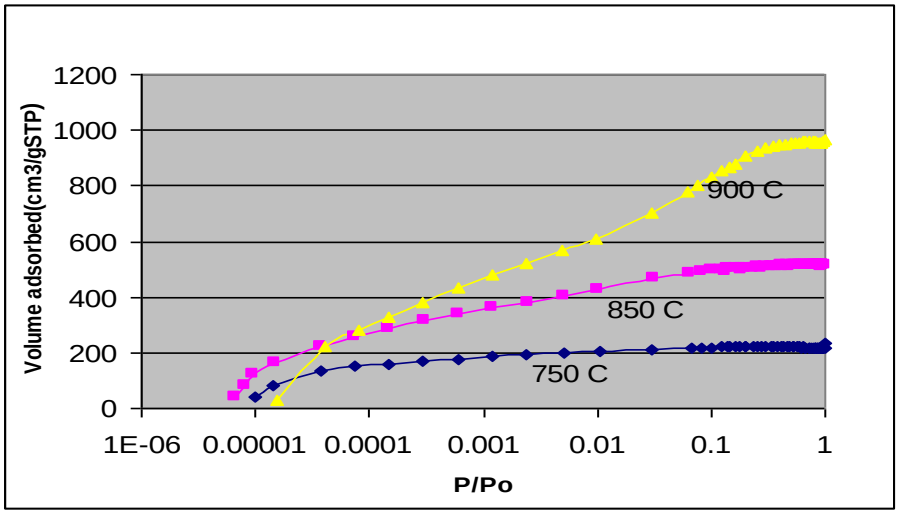


Figure 4.24: Nitrogen Isotherms for Carbon Fibers Activation at Different Temperatures (Semi-logarithmic Scale)

All of the above isotherms are type I, and the width of the knee increases strongly with increasing burn-off. It is seen from logarithmic scale nitrogen isotherms, as the activation temperature increase from 750°C to 900°C, the slope of isotherms increase.

The semi-logarithmic scale of activated carbon fibers at 900°C shows linearity. This means that at low pressures, adsorbed volume is totally due to microporosity. After P/Po ratio of 0.1, the adsorbed volume shows a clear increase which is attributed to the adsorption to mesoporosity, macroporosity and external surface area of the sample [66].

Although the adsorption isotherms for all samples are similar, the adsorption capacities are significantly different according to the activation temperature. These results indicate that the process conditions have significant influence on the porosity development of activated carbon fibers.

The results of pore size distribution of density functional theory (DFT) for carbon fibers activated at 750°C, 850°C are given in Figure 4.26 and Figure 4.27 respectively and pore size distribution for carbon fibers activated 900°C is given in Figure 4.16.

From the Figure 4.25-a, and Figure 4.25-b, the sample has cumulative volume of 0.18 cm^3/g, and formed with micropores. The pore width is measured between 8.04-15.91 angstroms. The dominant pore width is 8.04 angstroms.

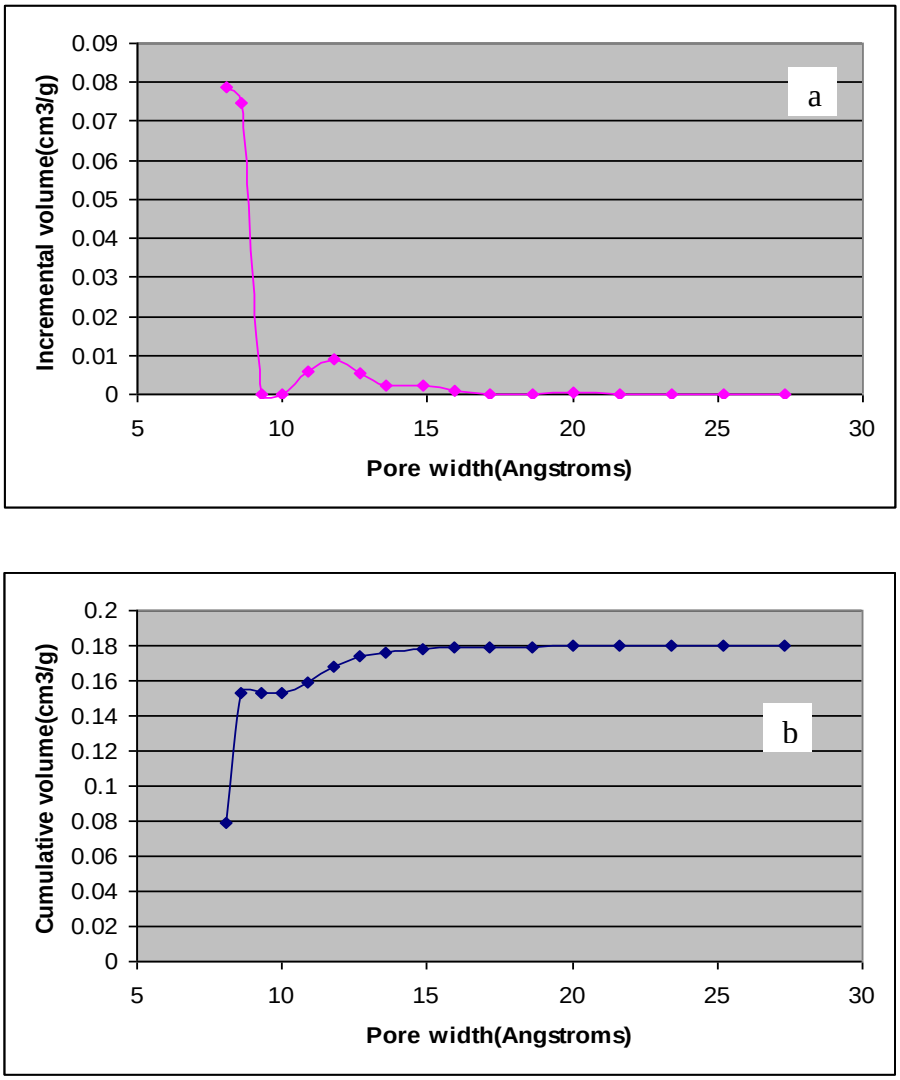


Figure 4.25 : Relationship between Incremental and Cumulative Pore Volumes with Pore Width of Carbon Fibers Activated at 750°C

From the Figure 4.26 a, b the sample has cumulative volume of 0,61 cm^3/g and it has only micropores. The pore width is measured between 7.33-15.91 angstroms. The dominant pore width is 7.33 angstroms.

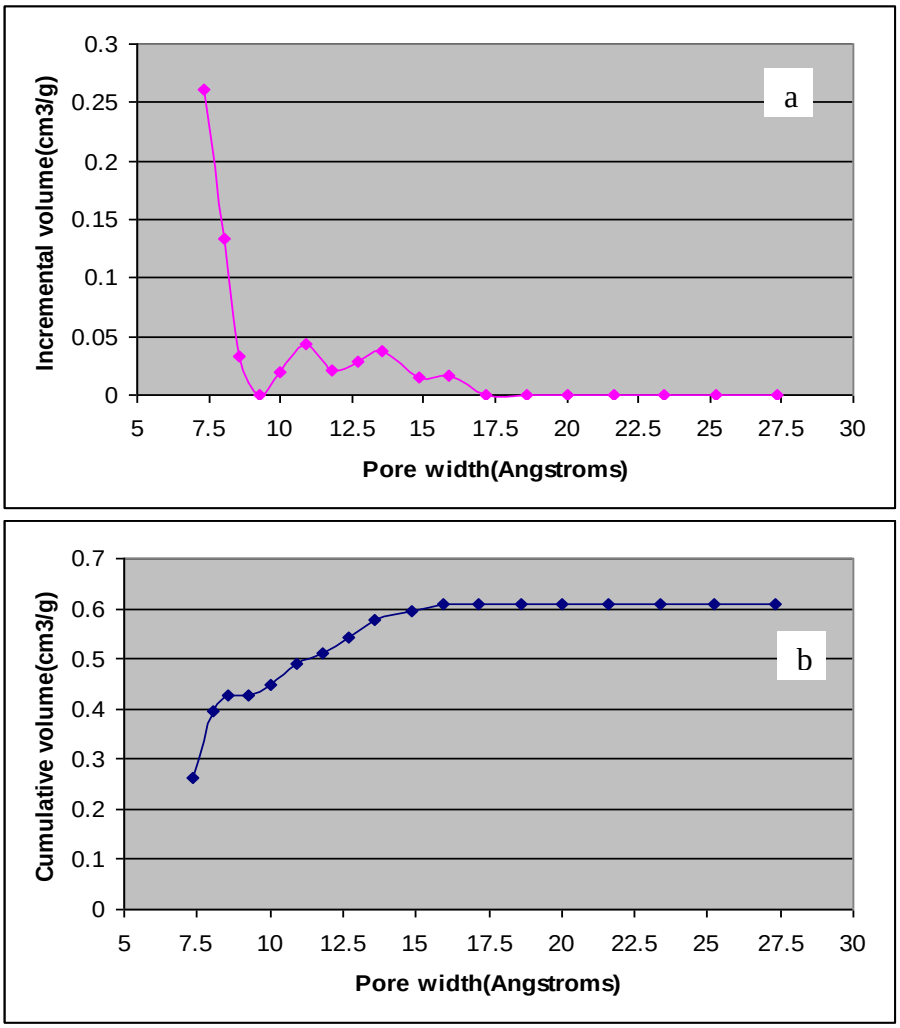


Figure 4.26: Relationship between Incremental and Cumulative Pore Volumes with Pore Width of Carbon Fibers Activated at 850°C

In order to understand the activation temperature effect on the pore volume, the pore volumes of carbon fibers activated at 750°C, 850°C, and 900°C are presented in Figure 4.27. As the activation temperature increase the micropore volume of the samples, and the interval of the pore size increase.

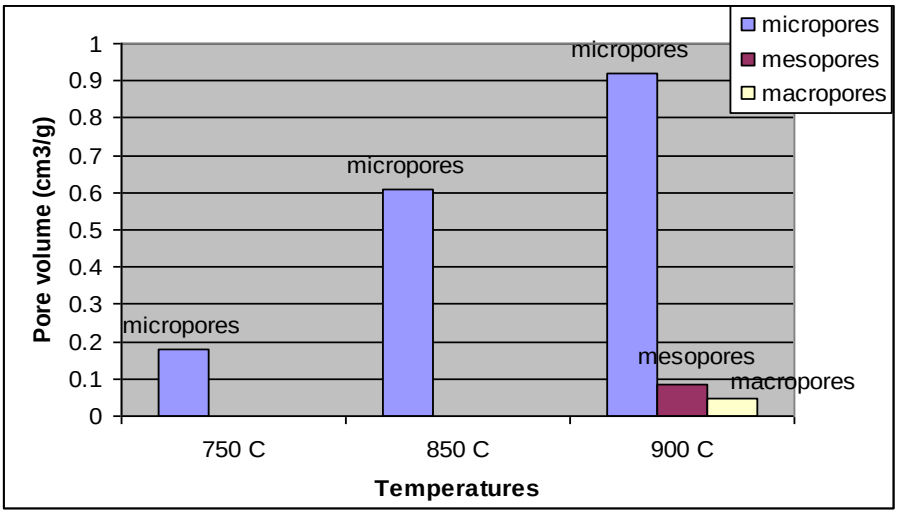


Figure 4.27: The Distribution of Pore volume with Micro, Meso, and Macropores for Carbon Fibers Activated at Different Temperature

To sum up, at low temperatures the creation of new pores is the dominant mechanism whereas at the higher temperatures creation of new micropore and pore widening occur concurrently.

In the light of recent growing interest in hydrogen storage and applications it is important to develop adequate and accurate methods for the characterization of porous materials that are designed for hydrogen applications [67],[68][69][70][71]

Due to the fact that hydrogen is supercritical at room temperature significant amount of hydrogen can only be stored at elevated pressures. However, hydrogen adsorption experiments performed at sub-atmospheric pressures can still provide important information about the hydrogen storage potential of an adsorbent material [69].

In this study, the hydrogen isotherm is performed at 77K. The hydrogen isotherms for the carbon fibers activated at 750°C, and 900°C are shown in Figure 4.28-a, and Figure 4.28-b, respectively .

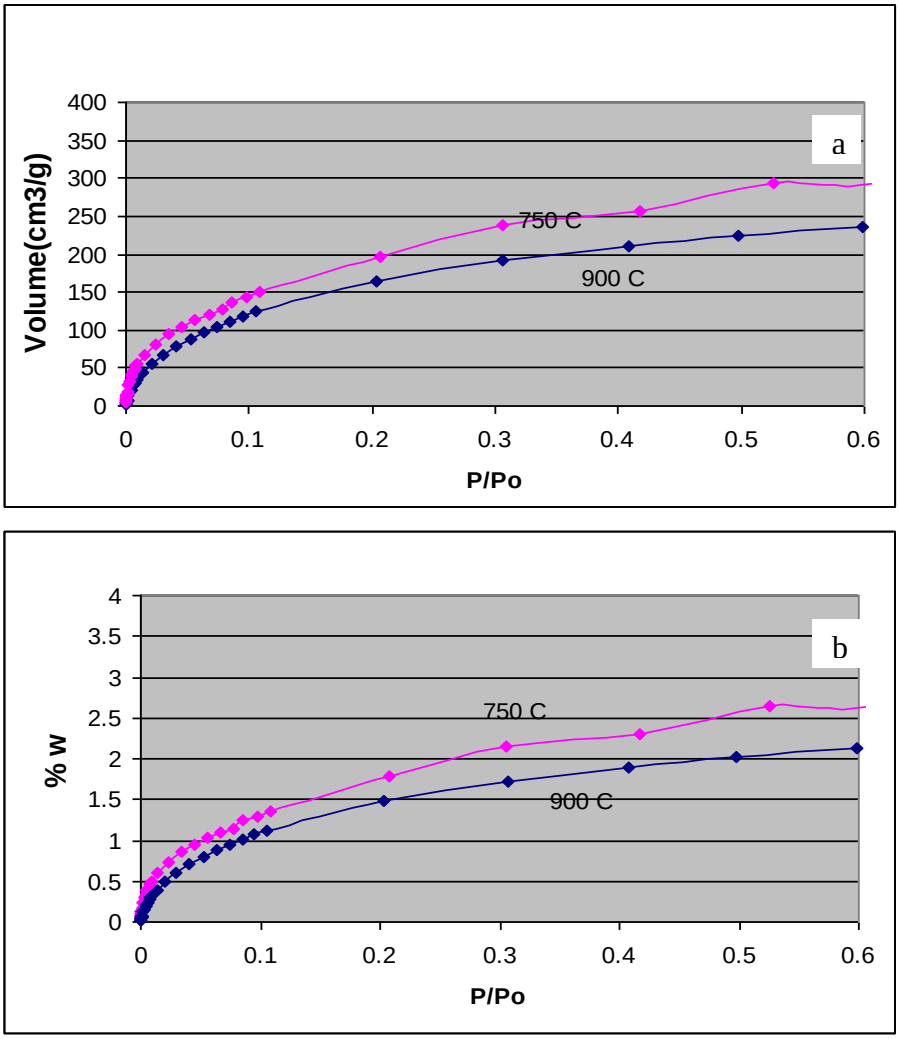


Figure 4.28 : The Hydrogen Isotherms for the Carbon Fibers Activated at 750°C, and 900°C a- P/Po-Volume b- weight %- P/Po

Hydrogen isotherms show that, carbon fiber activated at 750°C (2.65 %weight at 0.6 relative pressures) adsorbs more hydrogen than carbon fiber activated at 900°C (2.12 %weight at 0.6 relative pressures). Jacek and coworkers reported the hydrogen adsorption of phenolic based activated carbon fibers as 1.7 % weight at 0.6 relative pressures [67], [69].

In literature [67], it is shown that pore size distribution calculated for a selected carbon sample from hydrogen and nitrogen adsorption data have two important differences. Firstly, the pore size range described by the hydrogen based pore size distribution begins at a smaller value than the pore size distribution based on nitrogen data. Secondly, the pore volume curve calculated from hydrogen data for this carbon sample lies above the nitrogen curves. This is the consequence of the fact that

hydrogen pore size distribution of this carbon includes additional volume of ultramicropores which is not included in the nitrogen pore size distribution.

Magnitude of hydrogen adsorption at given temperature and pressure conditions, strongly depend on pore sizes, and so-called ultramicropores (pore sizes<7 angstroms) [67][69][70][71]. In this study, due to instrumentation limitation it is only possible to see the pores larger than 7.33 angstrom. However, the above mentioned hydrogen adsorption results indicate that there is substantial amount of ultramicropore formation smaller than 7 angstrom.

Carbon fiber activated at 750°C has less micropore volume (Figure 4.27) than the micropore volume of carbon fiber activated at 900°C. However Carbon fiber activated at 750°C adsorbs more hydrogen than carbon fiber activated at 900°C.The reason of this unexpected result may be explained by the presence ultramicropores on carbon fiber activated at 750°C. In literature [72] similar results are reported.

Results of using different probe molecules for isotherms give different results. Therefore the adsorbate gas should be selected appropriate with the pore size distribution of the materials.

4.5. The Effect of Chemical Treatment on the Properties of Resulting Activated Carbon Fibers

In this set of experiments, the carbon fibers are treated with different chemical agents such as H_2SO_4, H_3PO_4 and HNO_3 at 85°C for 2 hours. Chemically treated carbon fibers are washed with distilled water and dried then carbon fibers are physically activated with CO_2+ steam mixture at 850°C for one hour.

In order to determine the effect of chemical treatment on the carbon fibers properties, the treated carbon fibers are analyzed with TGA instruments. The results of H_2SO_4, H_3PO_4, and HNO_3 treated carbon fibers are shown Figure 4.29, Figure 4.30, and Figure 4.31 respectively.

TGA measurements are conducted using 30 mg sample, under argon atmosphere, from room temperature to 1000 °C with a heating rate of 10 °C /min.

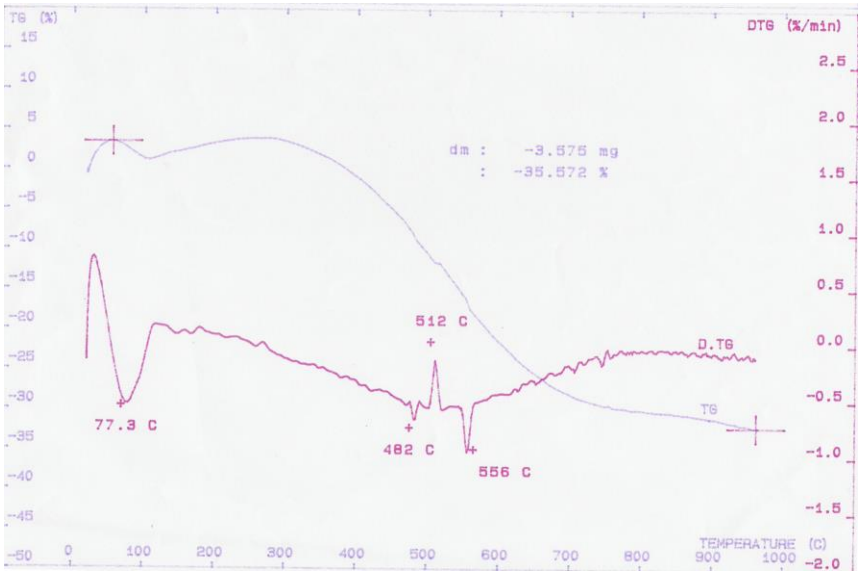


Figure 4.29 : Thermogravimetric Analysis of H_2SO_4 Treated Carbon Fibers

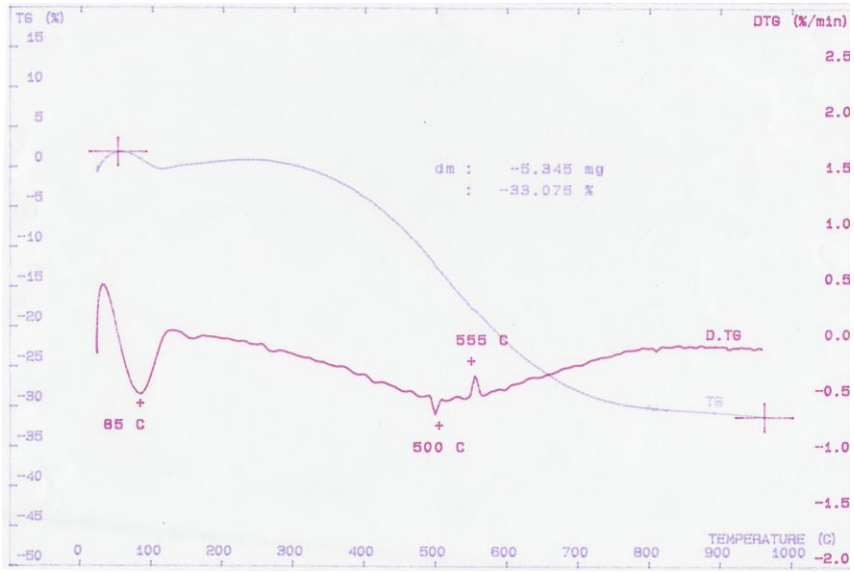


Figure 4.30: Thermogravimetric Analysis of H_3PO_4 Treated Carbon Fibers

Figure 4.31: Thermogravimetric Analysis of HNO_3 Treated Carbon Fibers

The carbon content calculated from TGA studies are compiled in Table 4.7. The evaluation of the table reveals that chemical treatment increases the carbon yield of carbon fibers.

Table 4.7 : Summary of TGA Studies for Chemical Treated Carbon Fibers

Samples	Carbon Yield (%) 0-1000 ° C
Green Carbon fiber	56.60
H_2SO_4 treated carbon fiber	64.43
H_3PO_4 treated carbon fiber	66.93
HNO_3 treated carbon fiber	66.25

H_2SO_4, HNO_3 and H_3PO_4 are strong oxidants, so they are selected as treatment reagents. The oxidation treatments generate the formation great number of oxygen-containing compounds and an increase of the oxygen content. However, on the following heat treatment step polycondensation reactions occur, and the oxygen content decreases [74].

With the increase of the temperature the chemical reagents decompose as follows.

$2H_2SO_4 \longrightarrow 2SO_2+O_2+H_2O$

$4HNO_3 \longrightarrow 2H_2O+4NO_2+O_2$

$4H_3PO_4 \longrightarrow 2PO_2+ 6H_2O+O_2$ [74].

Burn-off percentage is changed with using different chemical agents (Table 4.12). As can be seen from Table 4.8 the highest the burn-off value is obtained for CO_2+steam mixture activation of carbon fibers at 850°C (without chemical treatment). This consequence is similar with TGA results. However, comparing TGA results with burn-off for chemical treated carbon fibers the weight loss is increased for all chemical agents treated samples. Because of this reason it can be reasoned that both chemical treatment and physical activation can affect the activation process directly.

Table 4.8 : Burn-off Change with Chemical Treated Carbon fibers

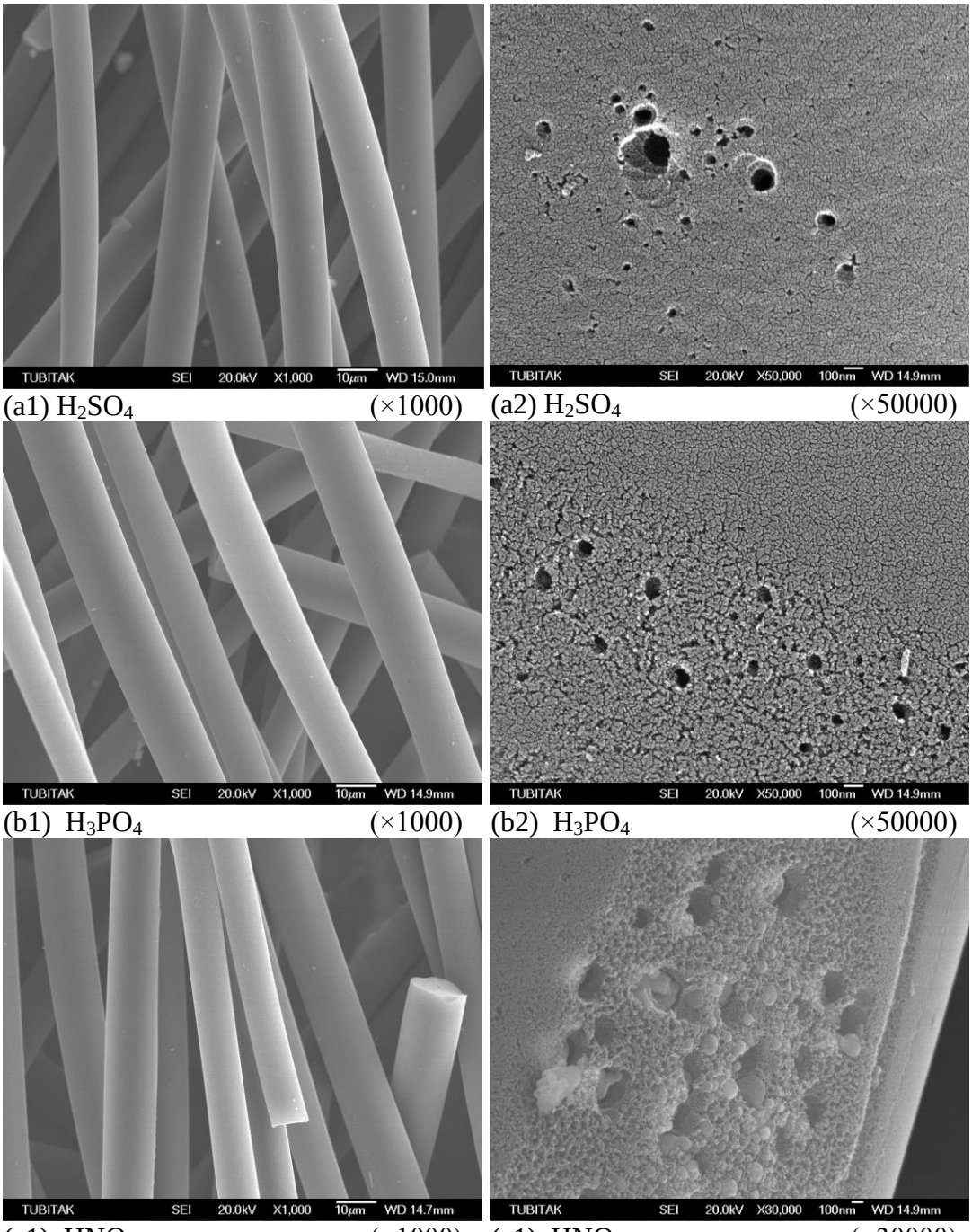
Chemical Agent	Burn off (%) (CO_2+ H_2O, 1 hour ,850°C)
H_2SO_4 treated carbon fiber	65.46
H_3PO_4 treated carbon fiber	66.75
HNO_3 treated carbon fiber	67.15
No chemical treated	70.00

The elemental analysis results of carbon fibers treated with different chemical agents are shown in Table 4.9. The elemental analysis results in Table 4.9 show that, the chemical treatment leads to an increase in oxygen content, and decrease in the carbon content of the activated carbon fibers. This is an indication of formation of a great number of oxygen containing structures during the thermo-oxidation treatment at 85 °C.

Table 4.9: The Elemental Analysis for Chemical Treated Carbon Fibers

Chemical Agent	(850 °C, 1 hour)	
	% C	% O
H_2SO_4 treated carbon fiber	83.40	16.6
H_3PO_4 treated carbon fiber	79.13	20.62
HNO_3 treated carbon fiber	86.02	13.2
No chemical treated	89.05	8.17

The SEM images obtained with 1000, 30000, and 50000 magnifications for chemical treated carbon fibers are given in Figure 4.32. From the high magnifications, macropore formations are observed on the surface. However, the distribution of macropores is not homogeny on the surface of the activated carbon fibers.



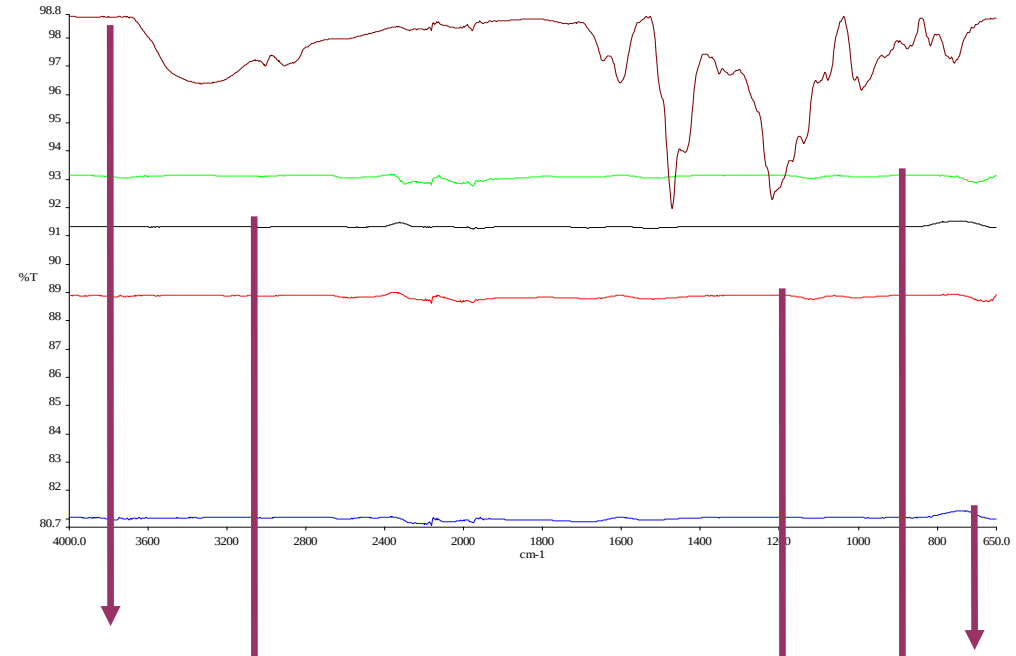
(a1) H_2SO_4 (×1000) (a2) H_2SO_4 (×50000)

(b1) H_3PO_4 (×1000) (b2) H_3PO_4 (×50000)

(c1) HNO_3 (×1000) (c1) HNO_3 (×30000)

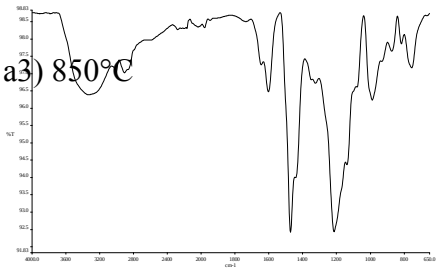
Figure 4.32: SEM Micrographs for Chemical Treated Activated Carbon Fibers

FTIR spectrums of carbon fibers chemically treated with various chemical agents are given in Figure 4.33.

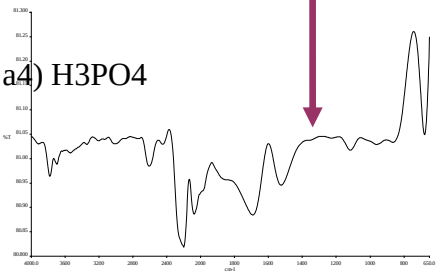


a1) Green Fiber

a2) H2SO4



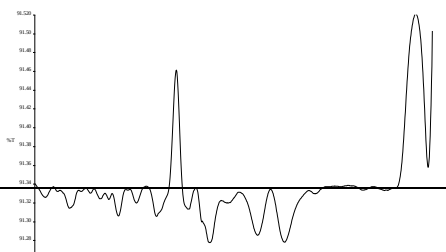
a3) 850°C

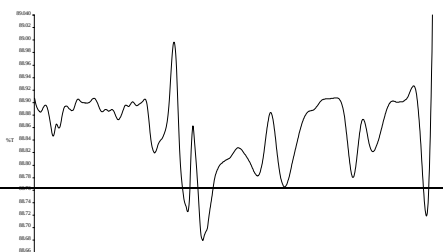


a4) H3PO4

a5) HNO3

Figure 4.33 : FTIR Spectrums for the Carbon Fibers Activation with Different Gases





The investigation of the FTIR spectrums showed that for various temperatures the samples have different spectrum with a more number of common peaks. The bands in the region of 1050-1200cm^{-1} are usually assigned stretching and bending of oxygenated groups. The bands at 1120 and 2150cm^{-1} is assigned stretching of ketene groups. 1950 such as in the band of 1200 is assigned stretching of alkenes.

BET surface areas of chemically treated samples are given Figure 4.34. As can be seen from the Figure 4.34 the micropore surface area decreases with chemical treatment. Although, there is both chemical and physical activation during these experiments, the expected increase for the surface area is not observed for chemical treated activated carbon fibers. The reason behind the discrepancy between the result and the expectation may be attributed to problems related with chemical activation procedure in which the chemical reactions is not caused porosity on process conditions. On the other hand chemical treatment cause increasing oxygen content and yield.

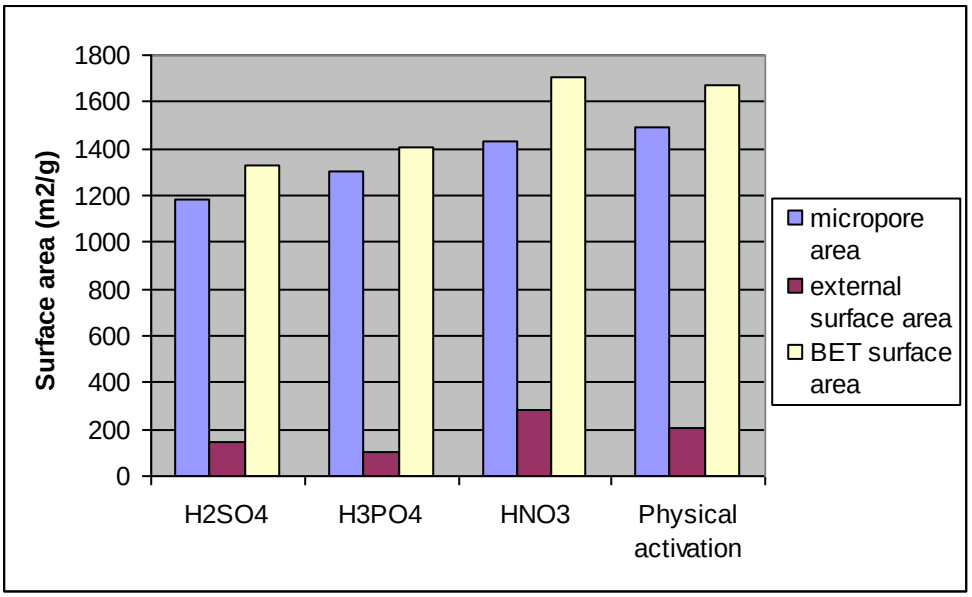


Figure 4.34: Surface Areas for Chemical Treated Activated Carbon Fibers

The nitrogen isotherms for the chemical treated activated carbon fibers are given in Figure 4.35, and Figure 4.36.

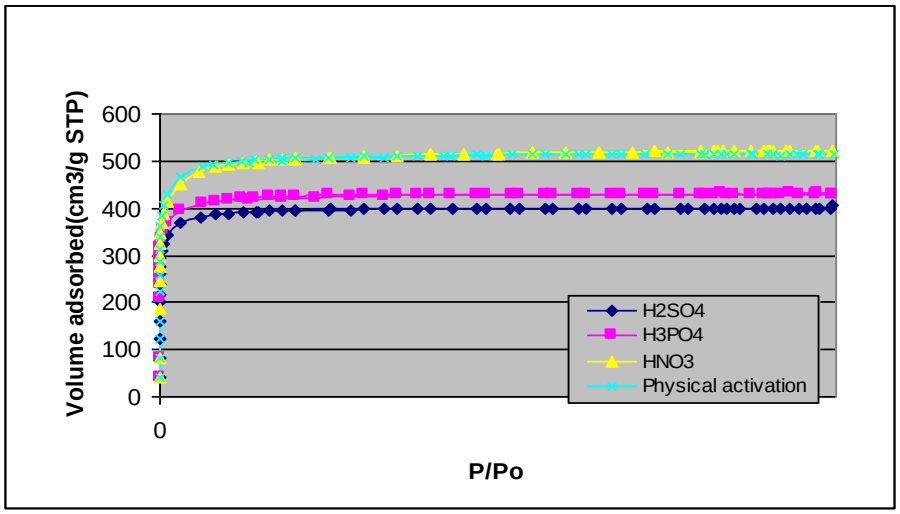


Figure 4.35: Nitrogen Isotherms for Chemical Treated Activated Carbon Fibers

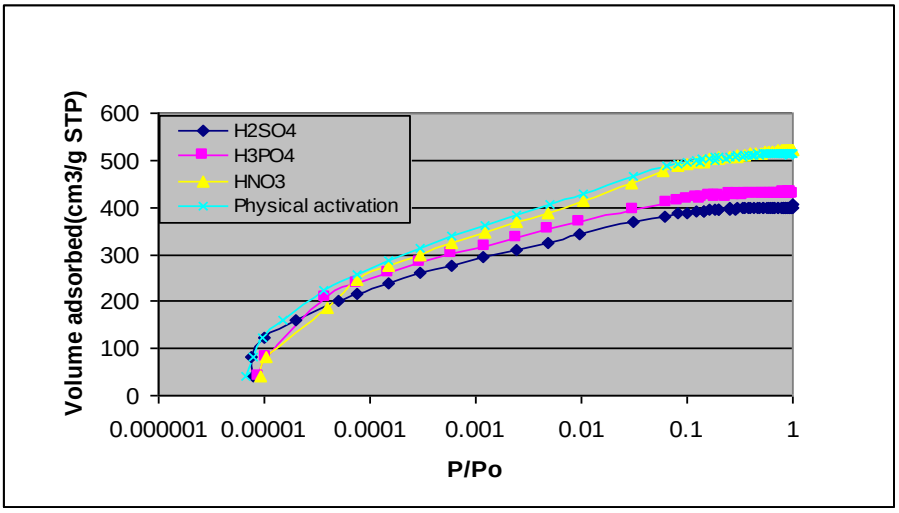


Figure 4.36: Nitrogen Isotherms for Chemical Treated Activated Carbon Fibers (Semi-logarithmic Scale)

Chemical treated activated carbon fibers and fibers activated by CO_2+steam mixture at 850°C present type I nitrogen adsorption isotherm as shown in Figure 4.35, and Figure 4.36. The results show the isotherms of activated carbon fibers obtained by treatment of different chemical agents show close similarities.

Incremental and cumulative pore volumes with pore width for chemical treated activated carbon fibers are given in Figure 4.37, and Figure 4.38 respectively. The similarities are exhibited those figures also.

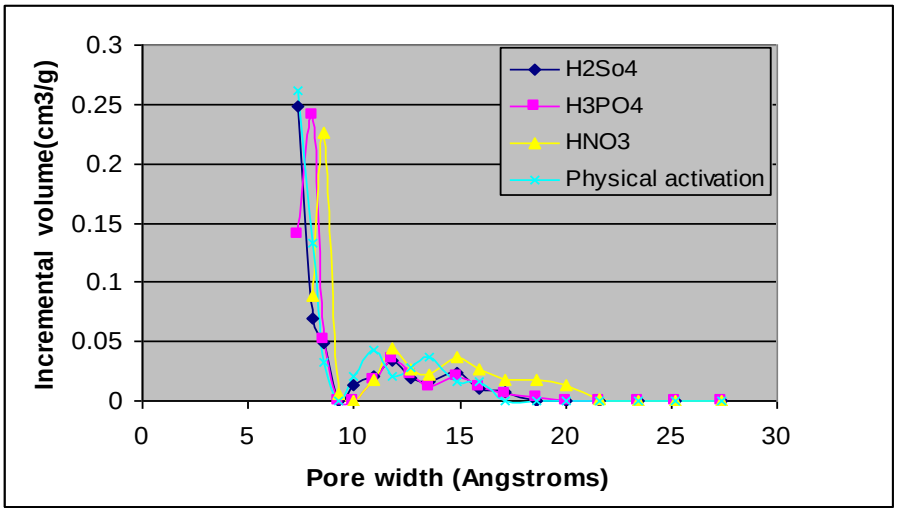


Figure 4.37 : Relationship between Incremental Pore Volumes with Pore Width for Chemical Treated Activated Carbon Fibers

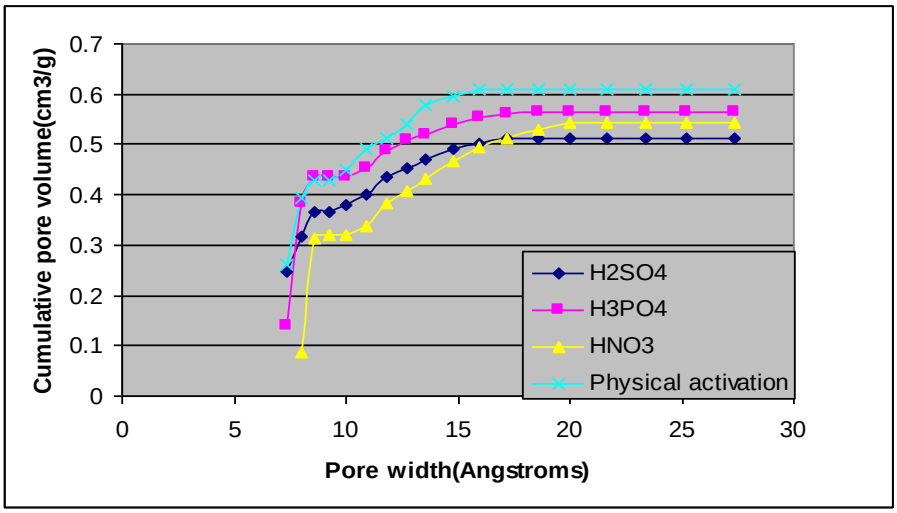


Figure 4.38 : Relationship Cumulative Pore Volumes with Pore Width for Chemical Treated Activated Carbon Fibers

The distribution of pore volume with micropores (<20 angstrom), mesopores (20<x<500 angstrom), and macropores (>500 angstrom) for chemical treated activated carbon fibers is given in Figure 4.39. As the figure show the volumes of chemical treated activated carbon fiber are less than the fibers activated physically.

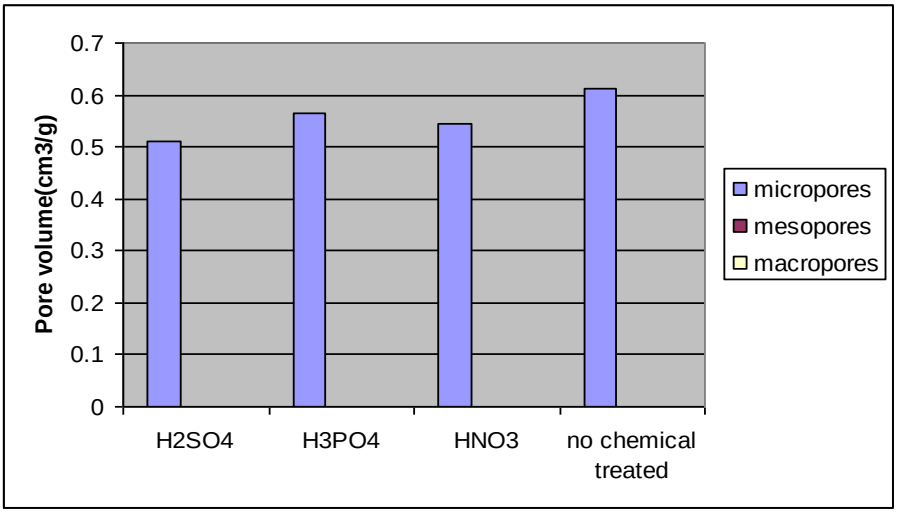


Figure 4.39 : The Distribution of Pore Volume with Micro, Meso, and Macropores for Chemical Treated Activated Carbon Fibers

To summarize one can say that chemical treatments do not affect pore size distribution and surface area, however increase the yield and oxygen content of the ACF. It is believed that chemical treatment cause crosslinking of the neighbor carbon atoms consequently make harder volatilization and decrease the surface area and pore volume.

5. CONCLUSIONS

The importance of carbon materials and carbon fibers is increased by their widening applications. In the present study phenolic based carbon fibers are activated using various activation techniques and their adsorption characteristics are investigated. The results and discussion of the various techniques and adsorption characteristics leads to the following conclusions.

1. Pre-washing of the carbon fibers with ethanol and methanol does not affect the following activation steps.
2. Burn-off percentage of the ACF increases, with time and temperature.
3. The values of carbon content, burn-off percentage, surface area, and micropore volume are in close relationship. The surface area increase causes increase all of the other parameters.
4. The synergetic effect of two gases is observed resulting highest porosity with the use CO_2+steam mixture. This mixture is found to be most suitable activation media.
5. The uses of Nitrogen and Argon for characterization of surface area of ACF give different results. The BET surface area calculated by the use of argon is higher for all activation gas type experiments in some order of magnitude compared the BET surface area calculated with the use of nitrogen.
6. Chemical treatment, decrease burn-off percentage and carbon content. The chemical treatment does not improve the porosity ACF.
7. It is found that phenolic activated carbon fibers have narrow pore size distribution with micropore structure and BET surface area up to 3000 m^2/g.
8. Activated phenolic fibers have a potential as adsorbent to be used, for various purposes. The ACF obtained at 750 C under CO2+ steam atmosphere give the highest (%3 percent (weight) hydrogen storage capacity.

6. RECOMMENDATIONS AND FUTURE WORKS

Investigation and characterization of activated carbon fibers produced by various processes are investigated and characterize in this study. As a result, many essential information is obtained. There is more room for further studies for better understanding the mechanism as well as to improve the properties of the material. Some of them are cited below.

1. Change the process and/or process stage for example chemical treatments without physical activation, chemical treatments after physical activation and investigate the properties of resulting ACF.
2. Trial of new processes and conditions in order to improve hydrogen storage capacity of the phenolic based carbon fibers. And conduct hydrogen adsorption experiments at different temperatures such as 87K and 283K.
3. Investigation of mechanical properties of activated carbon fibers for determination of possible application area.
4. Acid concentration should be studied in order to see the effect on ACF properties.
5. The adsorption performance of the ACF produced should be determined for various application areas (for example removal of NOx and SO2 from polluted air)

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CURRICULUM VITAE

Filiz KARADAĞ was born in Rize, in 1979. upon her graduation from Rize Anatolian High school, she entered Trabzon Yomra Science School. In 1997, she started Istanbul Technical University, chemical engineering department, in 2000, she started double major, industrial engineering department. In 2002, she graduated from chemical engineering department as the top student. After this, she started M.Sc studies at Istanbul Technical University Advanced Technologies Department, Material Science and engineering program. In 2005, she graduated from industrial engineering department. She got scholarship from TUBITAK, Finans vakfi, ITU Vakfi.